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QUALITY IMPROVEMENT OF FAST PYROLYSIS BIO-OIL THROUGH ALKALI REMOVAL FROM FEEDSTOCK

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Major in Biomass Refining

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Abstract of master's thesis

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Abstract: As the pressure to reduce greenhouse gas (GHG) emission grows, more interest towards sustainable bio-fuels emerges. Utilizable, non-edible and renewable waste streams are one of the most promising feedstocks to maximize the emission reduction. Fast pyrolysis is robust and rather simple liquefaction technique which can turn these solid feedstocks to high energy density liquid bio-oil. Although utilization of waste streams is one of the most potential ways to reduce GHG emissions, reduced quality of feedstock is problematic from the scope of the processing. Inorganic, ash forming elements of biomass, cause several problems during the fast pyrolysis process. Especially alkali and alkaline earth metals (AAEM) potassium, sodium, calcium and magnesium have been shown to possess catalytic activity, which results in decreased product yield and altered chemical composition of produced bio-oil. In addition, larger inorganic content in feedstock results in higher inorganic concertation in bio-oil, which is problematic from the scope of the further processing. Thus, pretreatment of low quality feeds, i.e. feeds with high ash content, has awaken interest.

Water and dilute nitric acid washing of biomass were studied with pine forest residues, eucalyptus and wheat straw grinded to particle size 0.55 - 0.98 mm. The effect of several parameters to total ash and AAEM removal were investigated. Although a large part of potassium and sodium were removable with water, the acidic washing liquid was more efficient regarding the total ash and AAEM removal. Especially removal of ion-exchangeable cations, such as calcium, was enhanced when acid washing was used. Changing parameters had varying effects within the raw materials. In the case of eucalyptus, elevated temperature and higher acid concentration were more efficient, whereas in the case of forest residues and especially with wheat straw, milder washing conditions were as efficient.

Regarding the raw materials, wheat straw was identified as the most promising feedstock to washing due to its high AAEM content and mildness of treatment conditions. Especially washing of the whole straws without grinding is interesting option which needs to be studied further. In addition, suitable AAEM levels in feeds should be clarified from the scope of bio-oil yield and quality maximization so that appropriate washing method could be chosen.

Keywords biomass inorganics, alkali metals, alkaline earth metals, biomass ash, alkali removal, metal removal, biomass washing, water washing, acid washing, pyrolysis, bio-oil.

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Tiivistelmä: Kasvava paine vähentää kasvihuonekaasupäästöjä on lisännyt kiinnostusta kestäviä ja ympäristöystävällisiä biopolttoaineita kohtaan. Uusiutuvat ja syömäkelvottomat jätevirrat ovat yksi potentiaalisimmista raaka-aineista päästövähennysten kannalta. Nopeapyrolyyysi on prosessi, joka mahdollistaa näiden kiinteiden raaka-aineiden jalostamisen nestemäiseksi korkean energiatiheyden omaavaksi bioöljyksi. Vaikka jätevirrat ovatkin potentiaalisia päästövähennysten kannalta, sisältyy heikkolaatuisten raaka-aineiden prosessointiin myös ongelmia. Lignoselluloosapohjaisten raaka-aineiden sisältämän epäorgaanisen aineosan, eli tuhkan, on todettu omaavaan katalyyttisiä ominaisuuksia pyrolyysiprosessissa. Erityisesti kaliumin, natriumin, magnesiumin ja kalsiumin on todettu vaikuttavan tuotetun bioöljyn kemialliseen koostumukseen ja saantoon. Lisäksi osa epäorgaanisista aineista päätyy tuotettuun bioöljyyn, millä voi olla vakavia haittavaikutuksia jatkojalostuksen kannalta. Tästä johtuen heikkolaatuisten, eli korkean tuhkapitoisuuden omaavien raaka-aineiden esikäsittely ennen pyrolyysiä on herättänyt mielenkiintoa.

Biomassan vesi- ja happopesuja tutkittiin metsähakkuutähteillä, eukalyptuksella ja vehnän oljella, jotka oli jauhettu ja seulottu partikkelikokoon 0,55 - 0,98 mm. Erinäisten pesuparametrien vaikutusta tutkittiin biomassojen kokonaistuhkan, sekä alkali ja maa-alkalimetallien pitoisuuksien alenemaan. Suuri osa raaka-aineiden natriumista ja kaliumista olivat poistettavissa vedellä, mutta happopesu oli tehokkaampi kokonaistuhkan sekä mitattujen metallien konsentraatioiden alentamisessa. Erityisesti ioninvaihtomuodossa olevien kationien, kuten kalsiumin ja magnesiumin poisto tehostui happopesua käytettäessä. Muuttuvien parametrien vaikutus vaihteli pestyn raaka-aineen mukaan. Eukalyptuksen kohdalla korkean lämpötilan sekä happokonsentraation todettiin tehostavan pesua, kun taas metsähakkuutähteiden ja erityisesti oljen kohdalla miedommilla olosuhteilla päästiin yhtäläisiin pesutuloksiin.

Raaka-aineista vehnän oljen todettiin olevan kaikkein potentiaalisin pestäväksi sen korkean alkali ja maa-alkalimetallipitoisuuksien, sekä mietojen pesuolosuhteiden johdosta. Erityisesti kokonaisen oljen pesu on kiinnostava vaihtoehto jatkotutkimusten kannalta, mutta lisätietoa tarvitaan myös metallien raja-arvoista raaka-aineessa öljyn saannon ja laadun kannalta.

Avainsanat biomassa, tuhka, metallit, alkalimetallit, maa-alkalimetallit, alkalien poisto, metallien poisto, biomassan pesu, vesipesu, happopesu, pyrolyysi, bioöljy.

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LITERATURE PART

1 Introduction

Fluctuating oil prices and increasing pressure to reduce greenhouse gas emissions has led to growing interest towards sustainable biofuels. Utilization of non-edible lignocellulosic waste streams as feedstock is one of the most promising and sustainable routes to maximize the emission reduction (Röder et al. 2014). However, low quality waste streams are problematic from the perspective of the biomass processing and introduce the need for feedstock pretreatment (Carpenter et al. 2014).

Fast pyrolysis is one of the routes for biomass liquefaction awaking commercial interest (Meier et al. 2013). Components of lignocellulosic biomass (cellulose, hemicellulose and lignin) are thermally degraded in the absence of oxygen to high energy density liquid product called as bio-oil. From the scope of the pyrolysis process, inorganic plant nutrients and ash-forming elements, especially alkali and alkaline earth metals (AAEMs), are the main impurities in the lignocellulosic feeds (Bridgwater 2018). Inorganics reduce the yield and affect to the quality of bio-oil by catalyzing certain reactions during pyrolysis, and by increasing the metal content of produced bio-oil (Oasmaa et al. 2015, Leijenhorst et al. 2016). Quality of bio-oil is especially important when considering the further processing of it in existing oil refinery infrastructures (Talmadge et al. 2014).

Washing of biomass from inorganics has been studied already from the 90's century from the scope of biomass combustion. In the pretreatment of combustion feedstock, focus has been on the chlorine and alkali removal (Jenkins et al. 1996). In addition, metal removal from feedstock of pulping industry has awaken interest (Brelid et al. 1998). From the scope of fast pyrolysis, removal of AAEMs, i.e. potassium, sodium, magnesium and calcium, is the most crucial. The most utilized pretreatment methods to reduce the inorganic content are based on

the water or acid washing, which are gentle towards the structure of biomass (Carpenter et al. 2014, Liu et al. 2017).

This thesis reviews literature on the inorganics in biomass, their effects in the pyrolysis process and their removal methods from raw materials. In the experimental part, leaching efficiency of water and aqueous acid in removal of AAEMs from different biomass feedstocks (straw, eucalyptus and forest residues) is studied with the aim of clarifying their potential as a pretreatment for industrial bio-oil production

2 Fast pyrolysis of lignocellulosic biomass

Biofuel production from biomass has awaken a lot of interest mainly due to the abundance of cheap lignocellulosic feedstocks and their availability for biofuel production. Lignocellulosics include agricultural residues, different grasses, crops and woody materials. Fast pyrolysis is one of the utilized biomass liquefaction techniques. Lignocellulosic feedstocks and their thermal degradation as well as fast pyrolysis process and product bio-oil will be discussed in this chapter.

2.1 Chemical composition and structure of lignocellulosics

The major elemental constituent of biomass are carbon, oxygen, hydrogen, nitrogen and sulfur. Rest of the elements contribute to the biomass ash content. Ash is defined as a residue left after complete combustion of organic matter of biomass and it consists of inorganic non-combustible elements present in plants. Elemental composition of various biomasses are presented in Table 1.

Elemental composition of biomass feedstocks differs greatly from the elemental composition of fossil feedstocks. In biomasses, portion of oxygen is significantly larger compared to fossil resources. On the other hand, fractions of carbon and especially hydrogen are much smaller. Differing composition has naturally major effects to chemical composition of biomass-derived fuels (Talmadge et al. 2014). In addition, fresh biomasses embody large amounts of moisture in their structure.

Typical moisture contents for freshly collected biomasses vary between 30 - 60 w-% (Alakangas et al. 2000).

Table 1. Elemental composition of forest residues, wheat straw and eucalyptus in dry mass basis.

	Ultimate analysis w-% d.b.					
	C	H	N	O	S	Ash
Forest residues[a]	51.30	6.10	0.40	40.85	0.02	1.33
Wheat straw[a]	47.30	5.87	0.58	41.49	0.07	5.71
Eucalyptus[b]	51.20	6.00	0.20	41.69	0.02	0.77

References: a; Wilén et al. 1996, b; Kurkela 1996.

2.1.1 Chemical composition

The major chemical constituents of lignocellulosic biomasses are the three structural components cellulose, hemicelluloses and lignin. Other polymeric substances found in much smaller quantities are pectins, starch and proteins. In addition, small amounts of non-structural extractives and inorganics are present (Alén 2011).

Cellulose is linear amphiphilic homopolymer consisting of β-D-glucopyranose units linked to each other by 1,4-glycosidic bonds. Degree of polymerization of native cellulose can be up to 15,000 and due to the equatorially oriented hydroxyl groups, cellulose molecules have tendency to form strong inter- and intramolecular hydrogen bond networks and stable crystal structures. Due to its crystal structure, cellulose is chemically and thermally rather stable and hardly dissolves in any common solvents. However, the hydrophilicity of cellulose results in extensive swelling of fibers in polar liquids such as water. End groups of a polymer have distinct properties. Hemiacetal structure at the one end of the polymer is reducing and the other end with secondary alcohol groups is described as non-reducing end (Koch 2006). Cellulose content in biomasses varies between

30 - 45 % on dry mass basis (Alén 2011). Structure of cellulose molecule is presented in Figure 1.

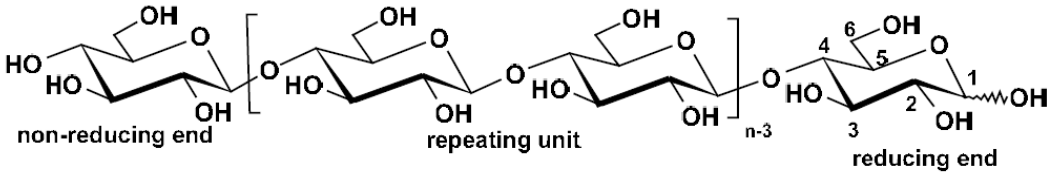

Figure 1. The molecular structure of cellulose (Koch 2006).

Hemicelluloses are heteropolymers consisting of different sugar monomers including glucose, mannose, galactose, xylose, arabinose and galacturonic acid residues. These building blocks link up to polysaccharides such as xylan, glucomannan, galactoglucomannan and arabinoglucuronoxylan by glycosisic bonds (Koch 2006). Composition and percentages of different hemicellulose components vary a lot with their botanical origin. Degree of polymerization of hemicelluloses is typically 100 - 300 and polymers are often branched and due to that completely amorphous. Functionality of hemicelluloses is more diverse compared to cellulose. For example, xylans have galacturonic acid side groups attached to its xylose backbone. Majority of hemicelluloses are either partly or completely water-soluble. Hemicelluloses make up approximately 20 - 35 % of biomasses on dry mass basis (Alén 2011). Structures of some common hemicelluloses found in woods are presented in Figure 2.

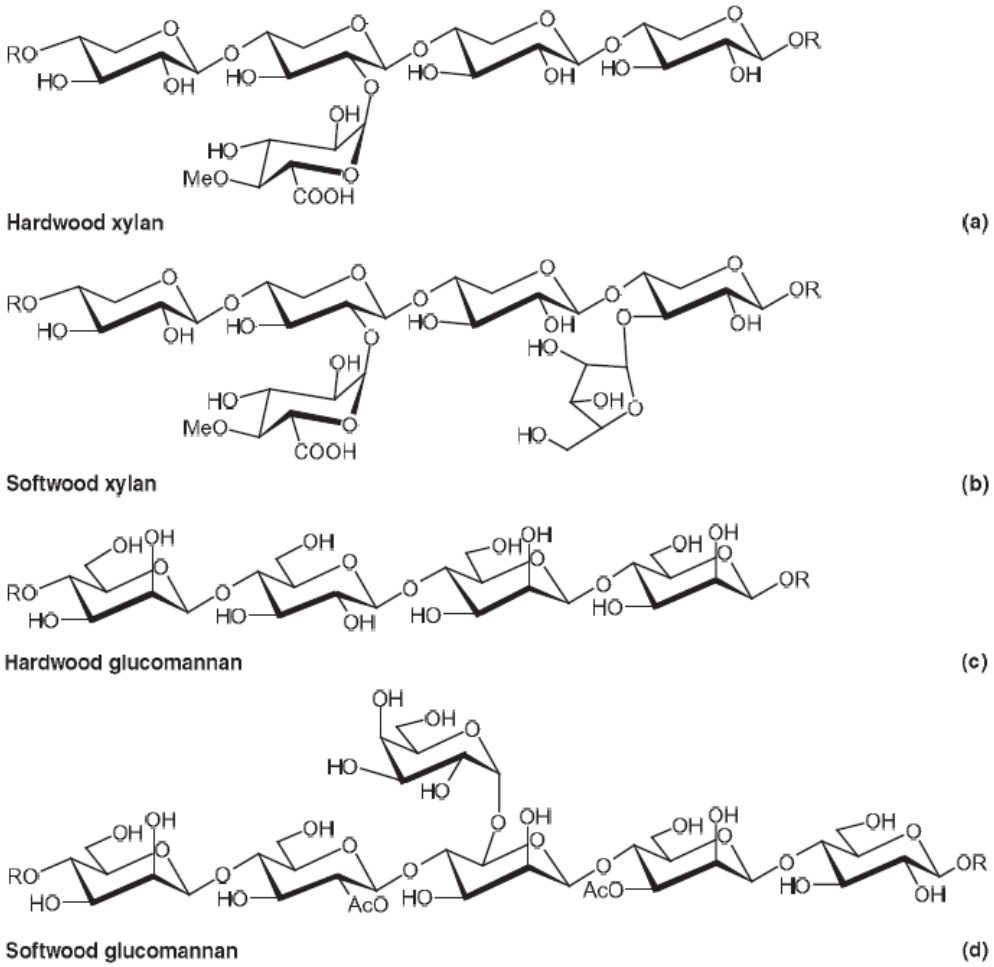

Figure 2. Molecular structures of hardwood xylan (a), softwood xylan (b), hardwood glucomannan (c) and softwood glucomannan (d) (Koch 2006).

The third structural component, lignin, has distinctly different chemical structure compared to other two major macromolecules. Lignin is amorphous polymer where monomers link to each other without precise order. Three main precursors of lignin are *p*-hydroxyphenylpropane, guaiacylpropane and syringylpropane. These precursors can bind with each other by several different carbon-carbon and carbon-oxygen bonds (Koch 2006). Structure of lignin precursors and common linkages between them are presented in Figure 3.

Lignins are typically divided to softwood, hardwood and grass lignin depending on the botanical source and distribution of lignin precursors. Softwood lignin consists mostly from guaiacylpropane units, hardwood lignin has approximately 50 %

guaiacylpropane and 50 % syringylpropane units, whereas grass lignin has typically roughly 40 % guaiacylpropane, 40 % syringylpropane and 20 % of *p*-hydroxyphenylpropane units. Lignin contributes 10 - 30 % of biomass on dry mass basis (Alén 2011).

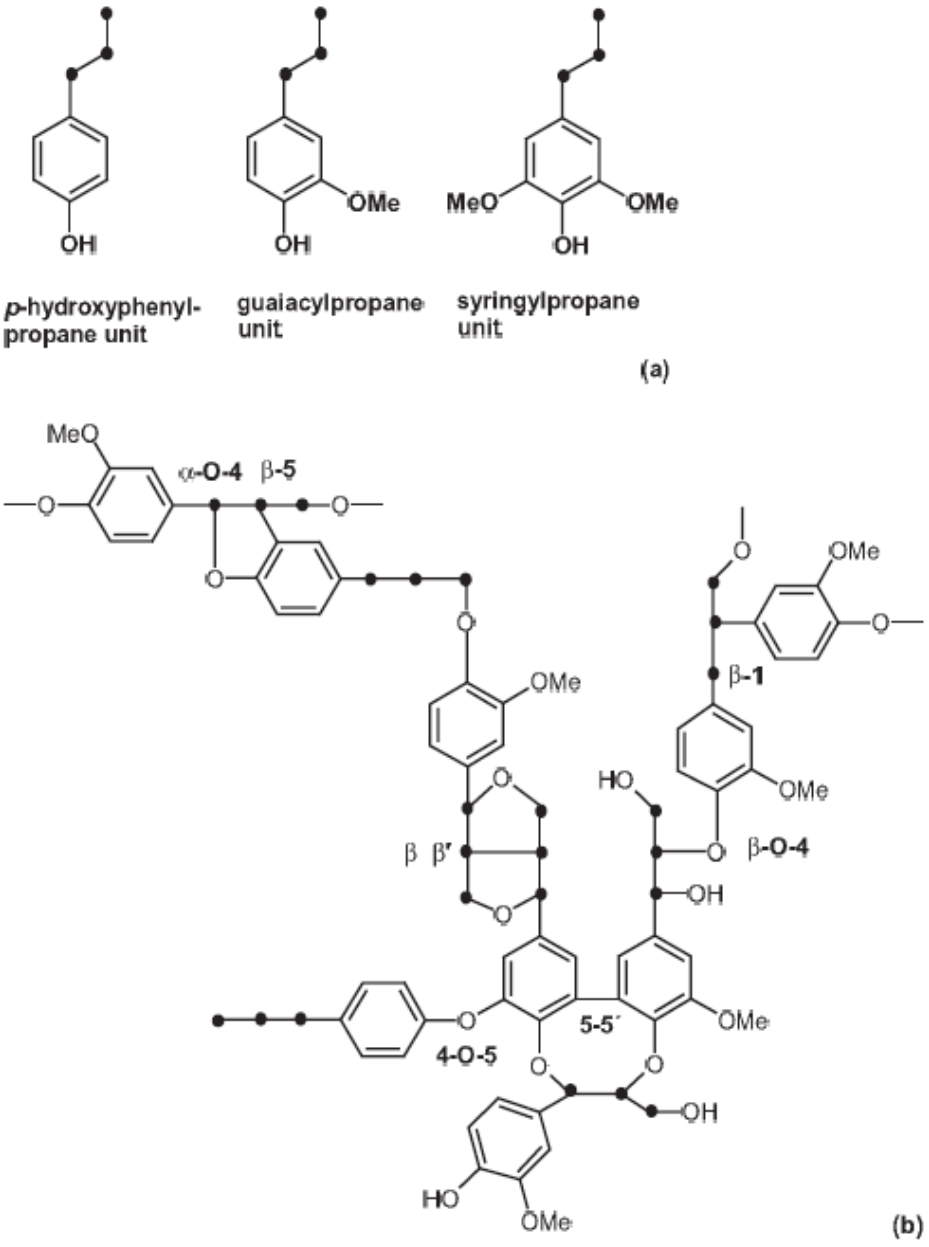

Figure 3. Molecular structures of phenyl-propane lignin precursors (a) and model of the important linkages in lignin molecules (b) (Koch 2006).

Other polysaccharides present in plants are pectins and starch. Concentrations of the polysaccharides are low, but they are important for plant physiology. Especially pectins bring acidic functionality to cell walls and are important components in middle lamellae binding plant cells together. Pectin consist partly of α-D-galactouronic acid units linked to each other by 1-4-glycosidic bonds (Sjöström 1981). However, pectic substances are complex in their structure that includes often other acidic residues and polymers, such as acidic galactans and arabinans (Alén 2011).

In addition to structural components, minor amounts of non-structural substances are present in plants for different physiological and biological reasons. These components are divided to extractives and inorganics. Extractives are large group of diverse organic components. Composition of extractives varies with the botanical origin of biomass. These components are usually small molecules and soluble to water or neutral organic solvents. Large portion of the extractives are biocides that protect plants against micro-organisms or insects. Extractives make up approximately 2 - 15 w-% of biomass on dry mass basis (Alén 2011).

Inorganics of biomass include elements such as alkali and alkaline earth metals, transition and post-transition metals and few non-metals. Concentrations of these components are low but many of them are essential micro- and macronutrients for plants (Marschner 2011). Content and concentrations of these elements vary a lot with changing source of biomass (Fengel & Wegener 1989). However, typical inorganics content in biomass varies between 1 - 10 w-% on dry mass basis (Alén 2011). Inorganics in biomass will be discussed in more detail in Chapter 3.

2.1.2 Structure of biomass

Chemical constituents of biomass are components of plant cell wall. Different components have different structural roles and their propositions are not uniform within the cell wall. For example, lignin and pectin concentrations are higher in the outer parts of cell wall and between the cells while polysaccharides are more abundant in inner parts. Although polymers and macromolecules interact mainly

with each other by hydrogen bonds and van der Waals interactions, some covalent lignin-polysaccharide bonds may exist (Koch 2006, Alén 2011). Structure of fibrils and cell wall are presented in Figure 4.

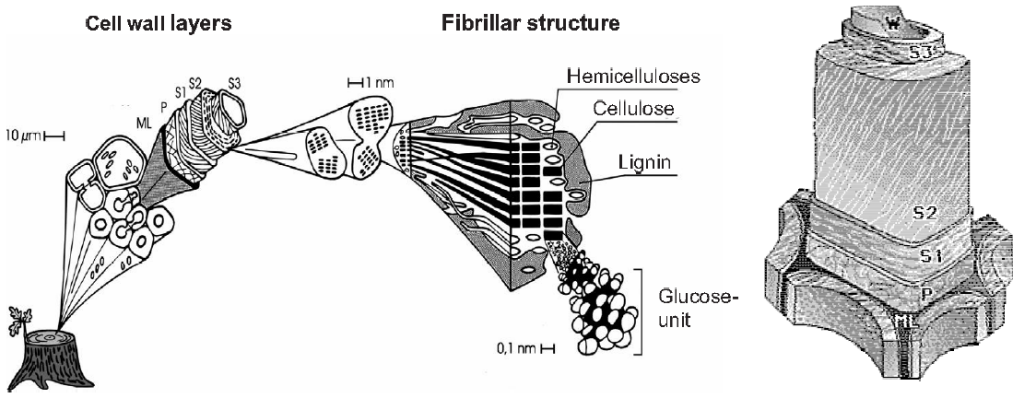

Figure 4. Structure of fibrils and cell wall (Koch 2006).

Cells are typically closed tubular structures and typically long compared to their thickness. Most of the cells are vertically aligned, but horizontal and axial cell structures exist for efficient fluid and nutrient transportation. Different types of cells exist in plants. Plant cells can be broadly divided to prosenchyma and parenchyma cells. Prosenchyma cells are thin, long and typically vertically aligned possessing mainly structural and conductive functions. Parenchyma cells are rectangular and shorter and they orientations are more diverse. One of the main functions of parenchyma cells is storing of organic and inorganic plant nutrients (Alén 2011).

Moisture of plants is trapped inside the cells as fluid and within the swollen cell walls but cells are connected in a way that allows the fluid flow through plants (Koch 2006, Alén 2011). Cell fluid is aqueous solution of various mobile organic and inorganic ions and non-charged species (Vassilev et al. 2012).

Only minority of plant cells are living and form biologically active tissues. Dead cells serve as mechanical support and as transportation pathways for water and nutrients to reach the living and growing parts of plant. Two different transportation tissue, phloem and xylem, exist in plants. Living cells are mainly in

phloem, located in the outermost layers of plant stem and in growing parts of plant. Majority of nutrients is transported in phloem to living cells. Rest of the cells are part of xylem, which acts mainly as water transport tissue, although part of the nutrients are also transferred in xylem (Koch 2006, Alén 2011).

Although the chemical composition and structures at cell level are rather similar in lignocellulosic feedstocks, significant physical differences exist in plants. For example, straws differ greatly from wood biomass. Straws have hollow structure and e.g. wheat straw has typically wall thickness of 0.3 - 0.7 mm (Willför et al. 2011). These varying physical properties will have effects in pretreatment at processes such as washing, drying, grinding and sieving.

2.2 Fast pyrolysis

Fast pyrolysis is one of the thermochemical conversions methods, including processes such as gasification and combustion. The aim in the fast pyrolysis is to produce high energy density liquid product, which could be used as fuel or as raw material for chemicals (Bridgwater 2010). Conventional thermal pyrolysis utilizes only heat in the liquefaction, but also catalytic pyrolysis has been developed to enhance the product quality (Paasikallio et al. 2014). Thermal and catalytic pyrolysis are briefly described in this chapter.

2.2.1 Thermal pyrolysis

Thermal fast pyrolysis is thermochemical liquefaction technique where solid feedstock is exposed to elevated temperatures in the absence of oxygen at atmospheric pressure. Feed material goes through thermal endothermic decomposition and vaporizes. Three products are obtained: char, liquid from condensable vapors and non-condensable gases. The product distribution can be altered by changing the process conditions. Lower process temperatures and longer vapor residence times favor the production of char. High temperatures and longer residence times increase biomass conversion to gas. Intermediate temperatures and short vapor residence time are optimum for producing liquids (Bridgwater 2010). The effect of reaction temperature on product distribution is

presented in Figure 5. Typically, lignocellulosic biomasses are used as feedstock, but for example, pyrolysis of waste plastics and municipal solid waste has also been studied (Wong et al. 2015).

In fast pyrolysis, reactions are rapid and occur in couple of seconds, reaction temperature being around 500 °C. When liquid yield is optimized, high heating rate is essential so that the exposure of biomass to lower temperatures is minimized. Typical heating rates are close to 500 °C/s (Bridgwater 2010). To achieve this high heating rate, small particles with diameter below 5 mm have to be used (Bridgwater 2010, Oasmaa et al. 2010). The moisture content of feed particles should not exceed 10 %, because the moisture ends up as water in the pyrolysis liquid with the pyrolytic water formed during the reactions. Thus, drying of the feed is usually necessary (Bridgwater 2018).

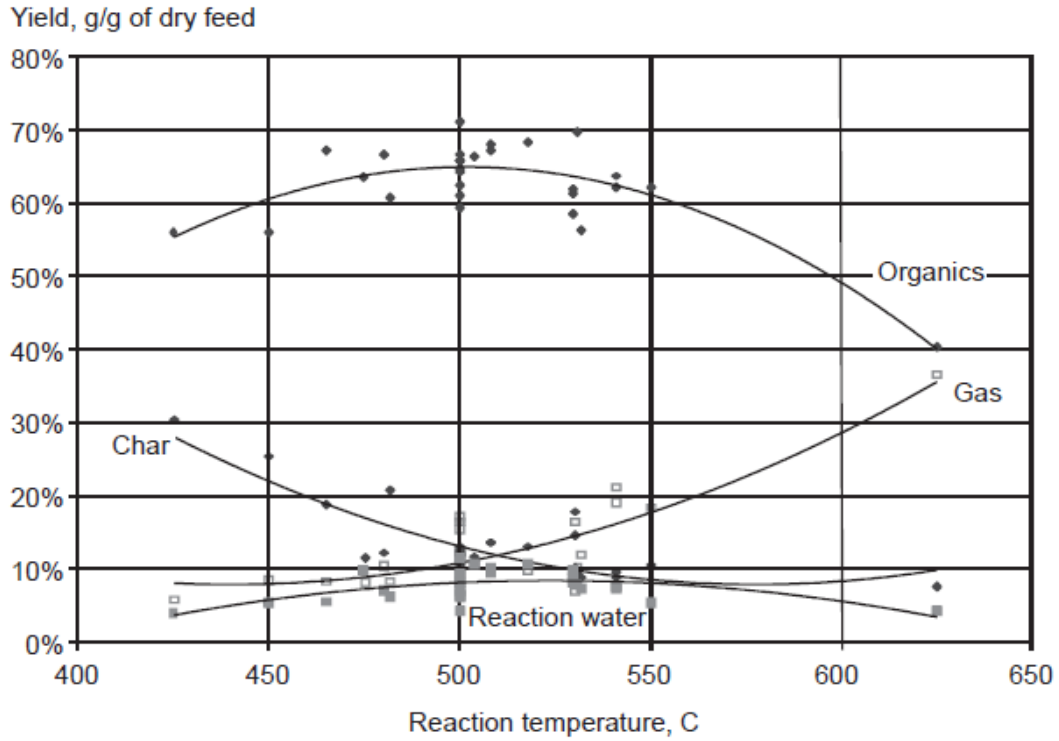

Figure 5. The effect of reaction temperature to product distribution in fast pyrolysis of aspen in dry mass basis (Bridgwater 2010).

After the pyrolysis reaction, solid particles are separated from the vapors and gases commonly with cyclones or hot-gas filtration (Baldwin & Fink 2013).

Separation of solids is followed by rapid cooling of vapors and gases to yield condensed pyrolysis liquid. Separation and condensation needs to be rapid, because ash particles and high vapor temperatures catalyze and enhance the formation of non-condensable gases and char with the expense of liquid yield (Bridgwater 2010).

Chars and gases contain typically 25 % and 5 % of the energy content of feedstock, respectively, and they can provide the heat needed for the process. Char consist largely from biomass inorganics and carbonized products derived from organic matter of biomass. Gases include carbon dioxide, carbon monoxide and traces of light hydrocarbons. (Bridgwater 2010).

One common configuration for pyrolysis unit is circulating bed reactor integrated with bubbling-bed combustor (Bridgwater 2010). The sand used to provide heat in pyrolysis is taken from the combustor and circulated back to it. Vapors formed during pyrolysis are collected, separated from solids and condensed. Char and non-condensable gases can be burned in combustor. Water content of bio-oil can be controlled to some extent by condensation temperature. Schematic figure of fluidized bed configuration is presented in Figure 6. Another commercial reactor type is rotating cone. In this reactor type, solids are separated from the vapors already in the cone shaped reactor. No high velocity carrier gas to fluidize the bed is needed and thus the separation of product vapors from solids is simpler and easier. Char and non-condensable gases formed in the reactor can be burned in similar manner as in circulating bed reactor to provide the heat for the process (Bridgwater 2010).

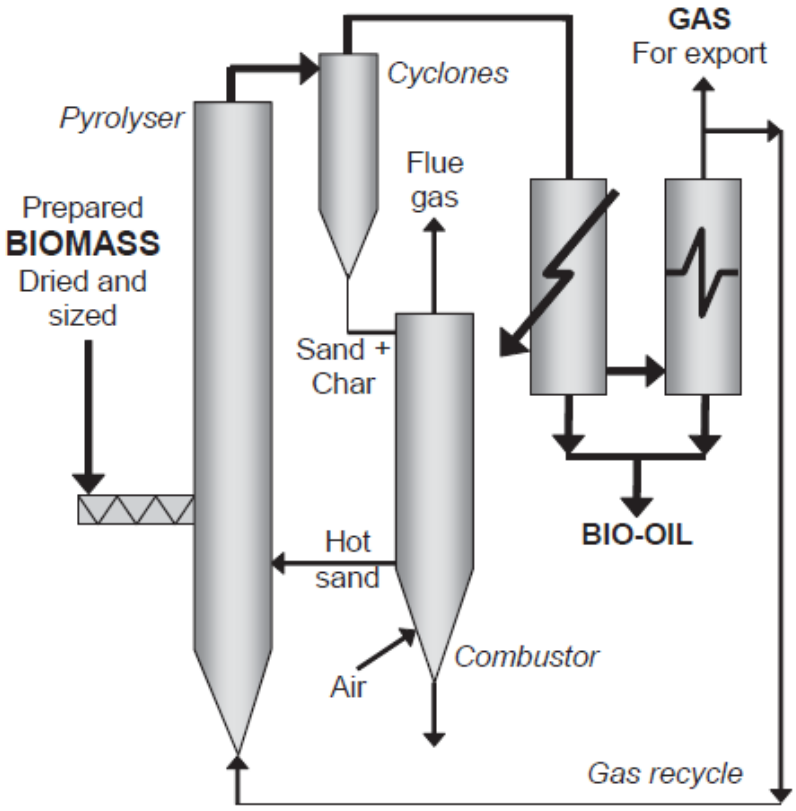

Figure 6. Typical configuration of circulating fluidized bed pyrolysis unit (Bridgwater 2010).

2.2.2 Catalytic pyrolysis

In addition to conventional thermal pyrolysis, catalytic pyrolysis is used to produce bio-oils. Process configurations are similar to thermal pyrolysis. Catalyst can be introduced with solid biomass, e.g. as heating material instead of sand, in the vapor phase as fixed bed or as fluidized bed in separate reactor (Mullen & Boateng 2013). The aim in the utilization of catalyst is to produce higher quality oils with lower oxygen content. Thus, the product oil is significantly different compared to oils from thermal pyrolysis. Catalysts typically used are acidic ZSM-5 zeolite catalysts (Mullen et al. 2017). Oxygen is removed as H_2O, CO and CO_2 by dehydration, decarbonylation and decarboxylation reactions (Paasikallio et al. 2014). Quality of the oil comes with the cost of oil yield due to the high oxygen content of biomass. Carbon yield is also reduced due to the decarbonylation and decarboxylation. Thus, water and gas yields are higher in catalytic pyrolysis.

Produced liquid goes through phase separation to organic and aqueous phase due to the large amounts of water produced and more hydrophobic nature of produced bio-oil (Paasikallio et al. 2014). Catalyst deactivation through coke formation and poisoning through accumulation of biomass inorganics on catalyst are common problems in catalytic pyrolysis (Mullen et al. 2017).

2.3 Thermal decomposition of lignocellulosic components

Thermal behavior of biomass components differs significantly from each other. Thermogravimetric analyzes by Yang et al. (2007) indicated that major weight losses with hemicelluloses and cellulose occur in temperature ranges of 220 - 315 °C and 315 - 400 °C, respectively. Lignin decomposition was more complex and challenging. Degradation of lignin occurred in wide temperature range of 160 - 900 °C. TGA results by Yang et al. (2007) are presented in Figure 7.

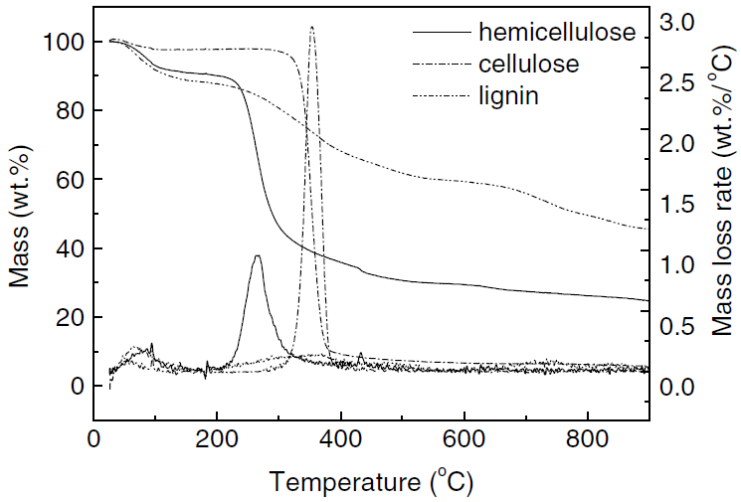

Figure 7. TGA of cellulose, hemicellulose and lignin (Yang et al. 2007).

Patwardhan et al. (2009, 2011a, 2011b) have studied comprehensively the primary product distribution from fast pyrolysis of pure cellulose, hemicellulose and lignin, respectively. Their results showed that the main product from pure cellulose was levoglucosan (1,6-anhydro-β-D-glucopyranose), with yield of 59 %. Other products from cellulose include water, char and gases as well as variety of different bio-oil components such as other anhydrosugars, oligosugars, furans, ketones, aldehydes and acids. These degradation products can be formed directly from cellulose or

through secondary reactions of the primary products (Parwardhan et al. 2011c). Widely accepted reaction mechanism for cellulose pyrolysis includes activation of cellulose to reactive intermediate, which can go through several competitive reactions such as end-group depolymerization by dehydration to anhydride intermediate and further to anhydrosugars or ring scission of monomer units to form char and gases (Patwardhan et al. 2009). In addition, repolymerization reactions of degradation products is possible. For example levoglucosan has been reported to repolymerize to form oligomers and components of char (Kawamoto et al. 2003).

Hemicellulose degradation is similar to cellulose degradation. However, pure hemicelluloses yield bit more char, gases, furans, ketones, aldehydes and acids and less anhydrosugars compared to cellulose. Yield of anhydrosugars is lower due to the high furanose content in hemicelluloses. For example, main products in xylan degradation are double dehydration products, because furanose degradation lacks the anhydride intermediate formation needed for reaction to anhydrosugars (Patwardhan et al. 2011a). Reaction schemes for cellulose and hemicellulose pyrolysis can be seen in Figure 8.

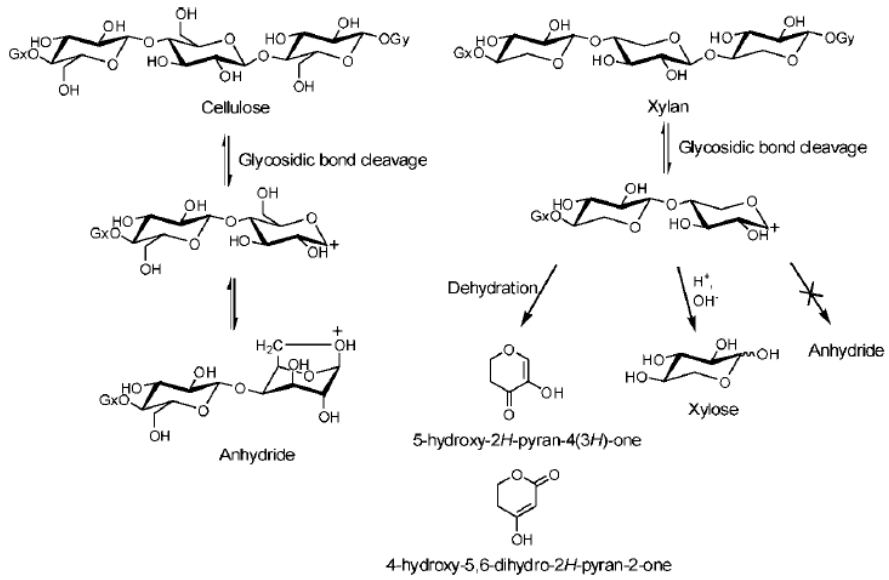

Figure 8. Proposed reaction mechanisms of cellulose and hemicelluloses under pyrolytic conditions (Patwrdhan et al. 2011a).

Results from pyrolysis of pure lignin indicate that its primary products are various monomeric phenolic compounds. In addition, significant amount of acids, aldehydes and ketones are formed. However, the vaporized phenolic compounds tend to recombine and form oligomers during condensation. Typically, 15 - 30 % of bio-oil consist of these oligomers called as pyrolytic lignin of varying molecular weight. Presence of acids has been reported to catalyze oligomerization reactions (Patwardhan et al. 2011b). Oligomers can end up to bio-oil also by thermal ejection through aerosol formation (Leijenhorst et al. 2016). Some pyrolysis products from lignocellulosics are presented in Figure 9.

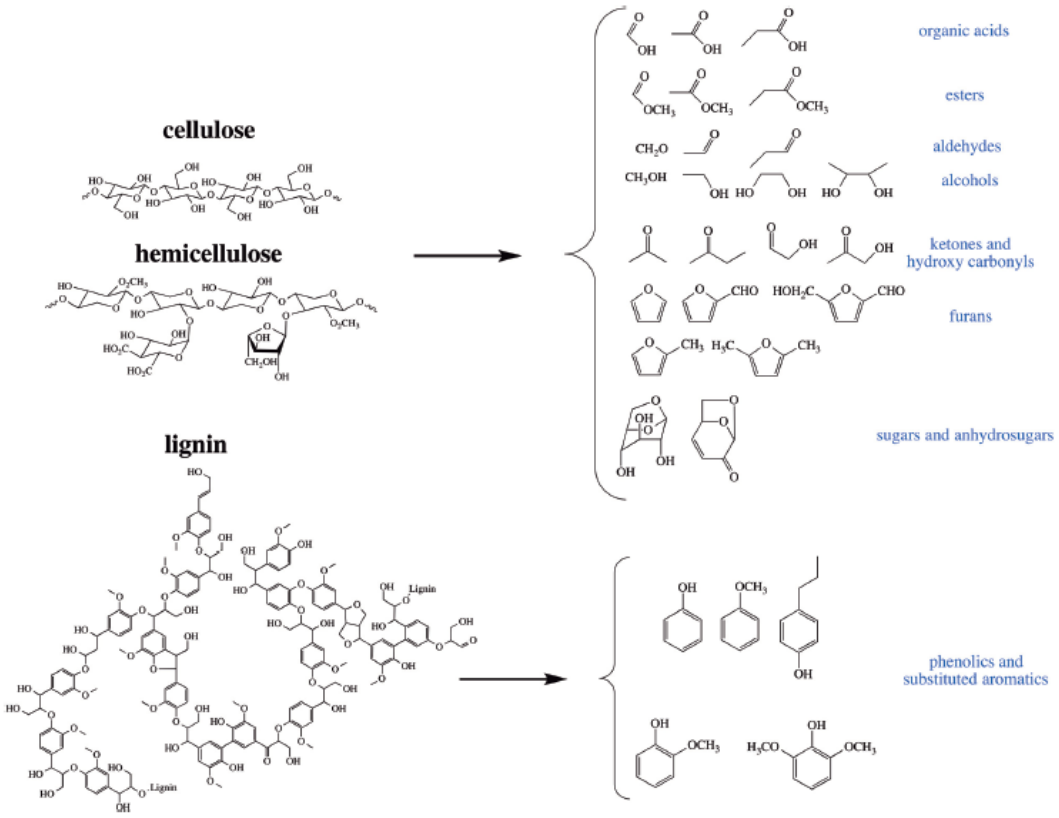

Figure 9. Typical pyrolysis products and bio-oil components from cellulose, hemicelluloses and lignin (Talmadge et al. 2014).

It should be emphasized that results presented above are for pure components in small scale. Real systems are more complex with larger amounts of potentially reactive species in vapor and liquid phases. For example, levoglucosan yield from pinewood pyrolyisis is commonly below 5 % (Oasmaa et al. 2015) meaning that

roughly maximum of 10 % of biomass cellulose is converted to levoglucosan. In addition, the inorganics of biomass catalytically promote certain reactions during pyrolysis (Bridgwater 2010). The effect of inorganics will be discussed in more detail in Chapter 4.

2.4 Bio-oil and its properties

In the fast pyrolysis the liquid is the desired product. This liquid is frequently referred to as fast pyrolysis oil, flash pyrolysis oil, bio-crude, bio-oil or fast pyrolysis bio-oil (Oasmaa et al. 2010). At best, biomasses with low ash content yield 75 % liquid, 13 % char and 12 % gases, but the yields vary with feedstock used (Bridgwater 2010). Some organic liquid yields of different feedstocks as function of temperature are presented in Figure 10.

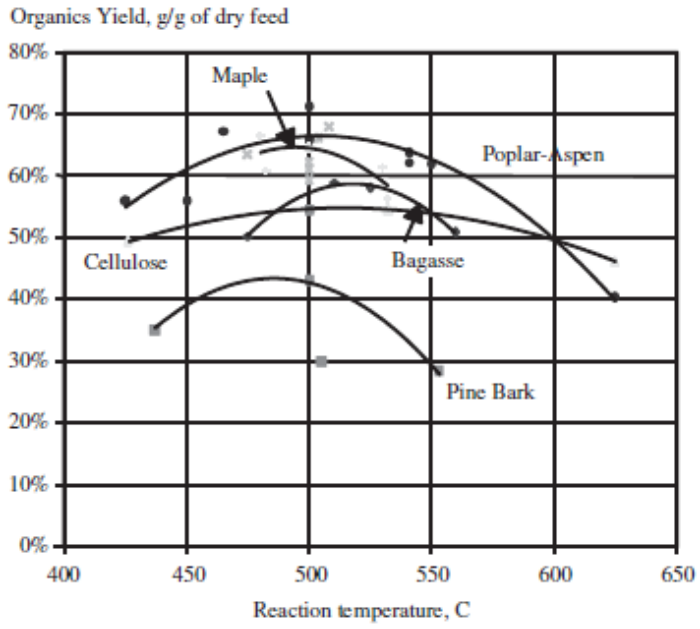

Figure 10. Yield of organic liquid fraction as function of temperature from fast pyrolysis of different biomasses (Bridgwater 2010).

Although the liquid is referred as bio-oil, its composition is far from conventional petroleum oil. Water content of bio-oil is typically 20 - 30 %, which includes the moisture of feed and pyrolytic water formed in dehydration reactions (Bridgwater 2010). The organic fraction consists mainly of oxygenated components due to the high oxygen content of biomass. Species such as aliphatic and aromatic acids,

alcohols, aldehydes, ketones, furans, pyrans, carbohydrates, sugar derivatives, pyrolytic high and low molecular weight lignin, extractives and polymerization products of these components are present in bio-oils (Oasmaa & Kuoppala 2003, Oasmaa et al. 2008). More than 200 components have been identified from these liquids (Diebold & Czernik 1997). In addition, some of the inorganic and solid substances of biomass end up into bio-oil. (Oasmaa & Kuoppala 2003, Oasmaa et al. 2008). The most abundant inorganics in bio-oils are AAEMs, iron and sulfur, which are present in varying ppm levels depending on the feedstock used (Baldwin & Fink 2013, Leijenhorst et al. 2016). Composition of different bio-oils can be seen in Figure 11.

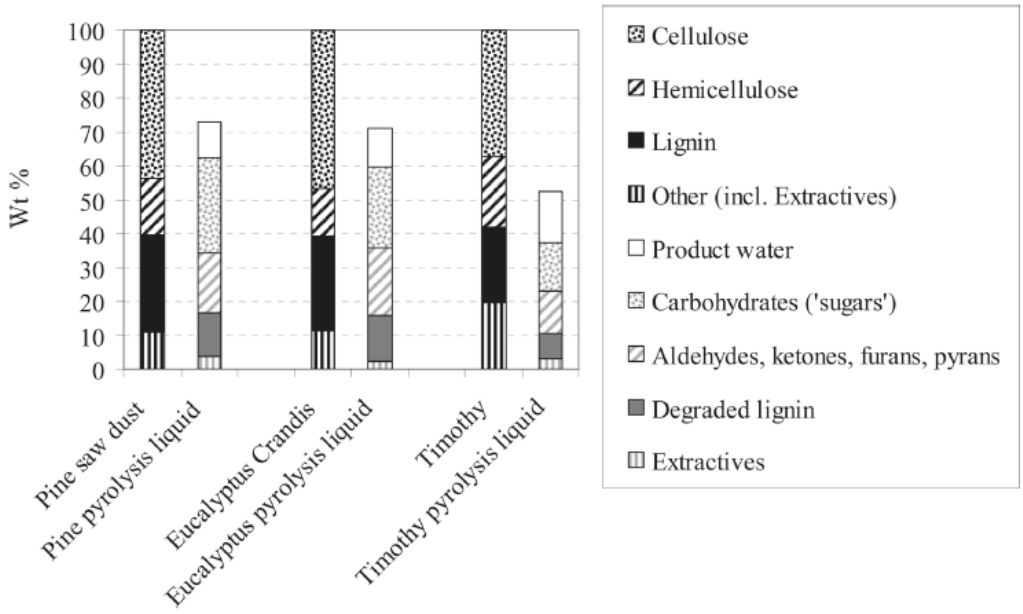

Figure 11. Compositions of bio-oils derived from different feedstock. Ash contents for pine saw dust, Eucalyptus grandis and Timothy grass were 0.1, 0.4 and 3.2 %, respectively (Oasmaa et al. 2010).

Large part of compounds in bio-oil are polar in nature and thus soluble in polar solvents (Diebold & Czernik 1997). Oasmaa et al. (2015) described bio-oil as a blend of three fractions. These fractions are hydrophilic fraction (i.e. water soluble but ether insoluble components), hydrophobic fraction (i.e. water insoluble components) and third fraction that acts as co-solvent for first two (i.e. water and

ether soluble components). When these fractions are in balance, bio-oil stays as homogenic one-phase system. However, if this balance is disrupted, two or more phases are separated.

The higher heating value of bio-oils is typically 17 MJ/kg with 25 % water content. Liquid is not distillable due to its instability and reactivity in elevated temperatures (Bridgwater 2010). Instability and aging of bio-oil through secondary reactions already in room temperature is also a well known phenomenon which leads to increased viscosity of liquid and possibly to phase separation. Aging needs to be taken into account when bio-oil is stored or transported (Diebold & Czernik 1997).

3 Inorganics in biomass

Inorganic content of biomass consist of many metals and non-metals. Over 60 different chemical elements have been detected from plants, 17 of them detected to be essential and several other to be beneficial for plant growth (King 2011). The most abundant inorganics in biomasses include elements such as Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn, and Ti (Vassilev et al. 2010). These elements can be divided into groups by their origin. Natural or physiological inorganics originate from soil nutrients taken up by plant during growth and are often minerals that plants physiologically need. They can be *authigenic* or *detrital*. *Authigenic* inorganics are formed in the biomass through plants metabolism and biogenic processes. *Detrital* inorganics are formed outside the biomass but fixed inside or on the biomass typically by wind or water suspensions. Anthropogenic inorganics are *technogenic,* meaning that they are introduced to plants during harvesting, handling and processing. For example, fine sand particles can be fixed on the plants surface in the pores and cracks (Vassilev et al. 2012).

Inorganic constituents of biomass, often referred as ash or ash-forming elements, contribute typically 1 - 10 % to biomass in dry mass basis (Alén 2011). Chemical composition and the amount of inorganics are highly dependent from the botanical source. For example, wood from temperate climates comprise 0.1 - 1 % ash, wood from tropical and subtropical climate can comprise up to 5 % of ash

(Fengel & Wegener 1989) and agro-residues can comprise up to 20 % of ash in worst cases (Baxter et al. 1998).

Higher growth rate of a plant is connected to a higher ash content. Thus, the inorganics content is often higher in younger plants during growing seasons. With trees, there is variation between different parts of the tree, ash content being higher in biologically active sections where nutrients are needed. For example, the living and the fastest growing parts, such as needles and leaves have higher ash content compared to bark, branches, roots and stem wood (Koch 2006, Davidsson et al. 2002). In addition, environmental conditions (site, climate, weather, soil) have significant effect on the concentration of inorganics. Salinity and metal content of soil correlates with the inorganics content of plants and vast precipitations reduce the ash content while dry seasons increase it (Baxter et al. 1998, Cohen & Dunn 2003).

Precise information on inorganic elements and their chemical statuses in biomass is scarce. Vassilev et al. (2010, 2012, 2014) have done statistical analyses regarding the chemical composition of biomass and its inorganics, but precise quantitative assessing of different components is challenging due to the high variations of ash content between the sources of biomass and their rather low concentrations. Ash-forming elements in biomass include alkali and alkaline earth metals, transition and post-transition metals, as well as non-metals. Inorganics are present in biomass as water-soluble ions, as salt precipitates, as minerals, in ion-exchangeable form and some form complexes with organic molecules (Brelid et al. 1998, Vassilev et al. 2012). The inorganic elements and their locations and binding habits in biomass will be discussed in the following sub-chapters. Some typical forms of the inorganics are presented in Table 2.

Table 2. Typical mineral forms of inorganics in biomass (Doshi et al. 2009).

Element	Ionic salts	Organically associated inorganics	Minerals
Na	Nitrates, Chlorides		
K	Nitrates, Chlorides		
Ca	Nitrates, Chlorides, Phophates	Calcium pectate	Calcium oxalate
Mg	Nitrates, Chlorides, Phophates	Magnesium pectate Chlorophyll	
Si	Amorphous silica		Phytolite, Quartz
S	Sulfur tetraoxide ion	Sulfolipids	
N		Amino acids, Proteins, Sulfolipids	
P	Phospate ion	Nucleic acids	Phytates, Phytic acid
Cl	Chloride ion		
Al			Kaolinite
Mn		Organic structures of proteins and carbohydrates	
Fe		Chelates, Organic sulfates	Phytoferritin, Iron oxide

3.1 Alkali and alkaline earth metals

Alkali and alkaline earth metals are the most significant inorganics in biomass due to their abundance and physiological functions. The most important AAEMs are potassium, sodium, calcium and magnesium, although the concentration of sodium is often much lower than that of the others (Koch 2006). Potassium, calcium and magnesium can make up to 80 % of inorganics in hardwood and softwoods (Alén 2011).

Potassium ions are essential for all living cells and they are usually quite mobile in plants (Smith & Shortle 1996, Marschner 2011). In plants, they are needed, e.g., in cell enlargement during the formation of new xylem cells (Koch 2006). Dominant form of monovalent alkali metals (K and Na) are ionic salts (Doshi et al. 2009). Potassium and sodium often dissolve as free ions (K^+ and Na^+) in fluid matter, and are trapped inside the cell structure of plants, with their counter ions. Part of K and Na deposits as solid salts on the cell walls of plants (Leijenhorst et al. 2016). Small amounts bound also into organic matter as carboxylates and phenoxides

(Marschner 2011, Vassilev et al. 2012). K and Na can also bind to organic phase due to ion exchange capacity of biomass (Davidsson et al. 2002).

Divalent alkaline-earth metals (Mg and Ca) are also essential nutrients for plant growth. However, their chemical status differs from alkali metals due to their different purpose in plants physiology. Both calcium and magnesium have stronger tendency to form complexes with organic counter ions instead of being in their free ionic form (Mg^{2+} and Ca^{2+}) (Marschner 2011, Keown et al. 2008). In general, magnesium is more mobile than calcium in plants, because calcium transportation occurs mainly by subsequent ion displacement inside the cell wall at apoplast. Magnesium is extensively transported in ion form in the fluid matter but also through subsequent ion exchange (Smith & Shortle 1996, Marschner 2011). In addition, alkali earth metals bind covalently with proteins and pectins (Doshi et al. 2009) and large part of calcium is trapped in ion-exchangeable form in middle lamellae of plant cells where it is needed in pectin synthesis and formation of "glue" that binds cells together (King 2011, Brelid et al. 1998). Calcium forms also minerals with oxalate and phytolith, which can enhance the structural properties of plants (Doshi et al. 2009).

Counter ions for AAEMs detected from biomass include chlorides, oxyhydroxides, phosphates, silicates, nitrates, carboxylates and sulfates. AAEMs can also bind with oxalates, carbonates and glucuronates (Vassilev et al. 2012, Koch 2006).

3.2 Transition and post-transition metals

When present in biomass, the concentration of transition metals, such as Fe, Cu, Ni, Cd, Cr, Co, Mn and Zn and the post-transition metals Al and Pb are usually low. Due to this reason, these elements are often referred as trace elements (Leijenhorst et al. 2016). However, iron can contribute up to 10 % to the ash-forming elements of wood and can be classified as macronutrient (Fengel & Wegener 1989, Marschner 2011).

Transition and post-transition metals are present in biomass in various different molecular structures. Determination of dominant structures is challenging due the

low concentrations of these elements. However, there is evidence that these metals can be in contact with organic matter as organometallic complexes, as impurities inside the amorphous or semi-crystalline cellulose, as impurities in salt-crystal structures and in ionic forms (Vassilev et al. 2014). In addition, presence of small metal crystal structures, probably originating from harvesting equipment, have been reported (Cohen & Dunn 2003).

Some transition metals are more evenly distributed within plant matter while others are more concentrated. More even distribution indicates that metals are predominantly in ion-exchangeable form instead of as inorganic insoluble precipitates (Räsänen 2000). Manganese is one example of evenly distributed ions while on the other hand, ferric ions (Fe^{3+}) have tendency to form hardly soluble salts with hydroxides and oxides. Large part of transition and post-transition metals have been reported to be in the corners of the cells and in middle lamellae, which is believed to result from the higher pectin concentration of these locations (Brelid et al. 1998).

3.3 Non-metals

In lignocellulosic materials, main non-metal inorganics are sulfur, phosphorus and silicon. Sulfur and phosphorus are both present in organic and inorganic components (Vassilev et al. 2012). The distribution between organic and inorganic species depends largely on the botanical source of biomass and location in the plants. For example, when complete wheat straw is considered, sulfur distributes almost equally between organic and inorganic components. However, when individual parts of the plant is considered, the roots show higher inorganic sulfate content, while sulfur in upper parts of straw is predominately in organic form. Reason for this is that plants absorb sulfur in inorganic form, further metabolize it, and produce organic substance such as proteins and amino acids (Knudsen et al. 2004). Sulfur and phosphorous are differently bound to organic macromolecules. Sulfur is predominantly in contact with hemicelluloses, while phosphorus favors contacts with lignin (Vassilev et al. 2014).

Metalloid silicon is also often present in relatively large quantities. Silicon is abundant elements in earth's crust and, e.g., sand consists largely from silica. Thus, silicon from plants may partly originate from dust and dirt (Vassilev et al. 2012) However, silicon is also beneficial to plants' physiology and it has structural significance through binding covalently with lignin and pectins. Silicon is absorbed from the soil largely as silicic acid, which interacts strongly with pectins and polyphenols, and is mainly located in the cell wall. Silica minerals formed in organic matrix of biomass can enhance plants' rigidity and structural properties especially in agricultural straws (Marschner 2011).

3.4 Solubility of alkali and alkaline earth metals

Several studies indicate that approximately 80 - 90 % of AAEMs in biomasses are in water- or acid-soluble form (Baxter et al. 1998, Davidsson et al. 2002, Scott et al. 2001, Mourant et al. 2011, Valmari 2000), K and Na being easier to remove with water than Mg and especially Ca (Mourant et al. 2011). This is logical due to the higher mobilites and different binding strengths of K and Na compared to Mg and Ca (King 2011, Smith & Shortle 1996). Water-soluble part is mainly water-soluble salts and free ions in fluid matter of plant. Acid soluble part can include salts and minerals only soluble in acids, but also water-soluble cations trapped in ion exchange matrix. Completely insoluble part of AAEMs might be insoluble salts or species strongly bound to organic molecules of biomass (Davidsson et al. 2002, Vassilev et al. 2012).

Majority of AAEM salts are soluble in water. For example, potassium chloride, potassium hydroxide and sodium chloride are highly water-soluble. In addition, potassium phosphate, nitrate and sulfate as well as magnesium sulfate and calcium nitrate dissolve in water. Some examples from poorly water-soluble species include calcium hydroxide, calcium oxide, calcium phosphate, calcium oxalate and magnesium phosphate. However, hydroxides and oxides react with acids forming water and free ionic species and phosphates of calcium and magnesium are soluble in acids (Renkonen 2016).

The ion exchange capacity of plant fiber is expected to result from the presence of carboxylic acid groups in polysaccharides, mainly in hemicelluloses and pectins (Brelid et al. 1998, Staccioli et al. 2000). Ion exchange capacity can be described with Donnan phenomenon. Cellulose fibers have strong tendency to absorb water and swell. Thus, the cell wall of plant can be thought as semi-permeable membrane, with inner and outer fluid solutions. Acid groups of polysaccharides can protolyze and release hydrogen ions, which leads to negative charge of polymer. This charge is stabilized by cation translocation into the inner fluid from outer one and cation concentration in fluids will reach equilibrium according to the present charges. pH of the solutions is crucial to the acid group protolyzation and thus also detrimental regarding the trapped cation concentration inside the cell wall matrix (Rudie et al. 2006). Thus, acids can remove ion exchangeable elements by two mechanisms. First, acid addition decreases the pH, which reduce the degree of protolyzation and the charge of the polymers, which subsequently reduces the cation concentration in inner fluid. Secondly, acids release H^+-ions which can replace the trapped cations in cell walls and release the inorganic cations to removable form (Brelid et al. 1998).

3.5 Inorganic content of straws, eucalyptus and forest residues

The concentrations of major inorganics found in different woody and agricultural biomasses are presented in Table 3. In general, straws have higher ash content compared to wood biomasses, although there is significant variation within these groups. Forest residues have higher ash content compared to stem wood of softwoods and eucalyptus. The most abundant ash elements are AAEM macronutrients calcium, potassium and magnesium with metalloid silicon. The most abundant transition metals are aluminum and iron. Non-metal macronutrients sulfur and phosphor are also present in significant quantities (Wilén et al. 1996, Morgan et al. 2016).

Major differences between ash content in woody biomass and agricultural waste seem to be lower relative alkaline earth and transition metal contents in agricultural feedstocks compared to woody biomasses. On the other hand, alkali

metals and silicon are more abundant in agricultural biomasses (Wilén et al. 1996, Morgan et al. 2016). Larger silicon content may be due to its larger structural significance in agricultural straws (Marschner 2011). Overall it seems that fraction of AAEMs is higher in woody biomasses than it is in agricultural straws (Wilén et al. 1996). However, it should be noted that ash content of biomasses varies a lot even within the same type of biomass.

Table 3. Proportions of most abundant ash elements of different woody and agricultural biomasses.

		Ash analysis, g / 100 g - ash								
Biomass type	Ash, w-%	Ca	K	Mg	Na	Si	Al	Fe	P	S
Wood										
Softwood chips[a]	0.60	24.0	10.0	3.1	0.2	11.0	2.7	1.5	2.1	0.7
Forest residue chips[a]	1.33	11.0	6.9	2.4	0.3	18.0	2.5	2.6	1.4	0.7
Saw dust (pine)[a]	0.08	29.9	10.2	7.1	0.2	3.9	1.0	1.3	2.3	0.8
Spruce (bark)[a]	2.34	28.0	6.3	3.1	0.3	0.7	0.5	0.1	1.8	0.4
Pine (bark)[a]	1.72	29.0	6.3	2.7	0.4	0.6	2.8	0.2	2.1	0.8
Eucalyptus[b]	0.7	28.6	14.2	5.7	5.7	2.9	2.8	5.7	14.3	1.4
Agricultural										
Wheat straw[a]	4.71	5.2	14.0	1.1	0.4	28.0	0.4	0.4	1.0	0.4
Barley straw[a]	5.88	3.2	16.0	1.3	0.4	29.0	<0.1	0.1	1.1	0.6
Rapeseed[a]	2.86	21.0	14.0	0.4	0.3	1.5	0.3	0.7	3.9	4.3
Flax[a]	2.93	24.3	19.9	3.1	0.3	1.7	0.4	0.4	6.7	1.5
Reed canary grass[a]	8.85	2.5	2.6	0.9	<0.1	42.0	0.8	0.8	1.8	0.5

References: a: Wilén et al. 1996, b: Morgan et al. 2016.

4 Effect of inorganics in pyrolysis

The catalytic effect of ash and inorganics in pyrolysis have been known for some time and even trace levels of certain elements have been recognized to have significant effects to the thermal degradation rates and pathways during pyrolysis (Evans & Milne 1997). AAEMs have been recognized to catalyze the biomass degradation to undesired directions and potassium is considered as the most significant and catalytically active impurity. In addition to AAEMs, phosphor and transition metals have been shown to have catalytic effects, but silicon is considered as inert material (Carpenter et al. 2014). Increasing ash content has been reported to decrease bio-oil yield (Fahmi et al. 2008, Oasmaa et al. 2015), induce phase separation (Oasmaa et al. 2015), change the chemical composition of bio-oil (Stefanidis et al. 2015), deactivate catalysts in catalytic pyrolysis (Mullen & Boateng 2013) and increase the inorganic content of bio-oil (Leijenhorst et al. 2016).

4.1 Catalytic effects on pyrolysis reactions

Changes in bio-oil composition and reaction pathways are reported to occur already in low ash and inorganics concentrations (Evans & Milne 1997, Patwardhan et al. 2010). Patwardhan et al. (2010) studied the effect of inorganics in primary pyrolysis products of pure cellulose. Cellulose was impregnated with different AAEM salts and switchgrass derived ash. All inorganic additives significantly enhanced formation of char and small molecular weight components such as glycoaldehyde, formic acid and acetol, with the expense of levoglucosan yield. Ash content already as low as 0.5 w-% had dramatic effects on the product distribution. From the individual cations, potassium had the most significant effect to levoglucosan yield followed by sodium. The effect of calcium and magnesium was milder in lower salt concentrations, but when more salts were added, differences were diminished. Authors speculated that inorganic metals might reduce the activation energy of competitive reactions from reactive cellulose intermediate and drive the reactions away from levoglucosan formation. Decreasing temperature was found to reduce the catalytical effects.

In the case of hemicellulose degradation, results have been similar. Char and gas yields have been reported to increase when metals are present. However, formation of small molecular weight components decrease, probably due to their further degradation to gases (Patwardhan et al. 2011a). In the case of pure lignin, no significant changes in primary product distribution were observed when samples were impregnated with inorganics (Patwardhan et al. 2011b). On the other hand, Oasmaa et al. (2010) reported that lignin was cracked more with high ash feedstocks and produced bio-oil included less high molecular mass lignin.

Stefanidis et al. (2015) and Mourant et al. (2011), who compared the chemical composition of bio-oils from de-ashed feedstocks to original ones, presented similar results. Major effects were seen on the sugar concentrations, which were significantly lowered in the presence of inorganic cations of biomass. Concentrations of C=O compounds in bio-oil, such as furans and ketones, were increased which indicate that metals can catalyze the homolysis of pyranose rings to carbonyl compounds in the expense of anhydrosugar formation (Stefanidis et al. 2015). In addition, de-ashed feedstocks resulted in lower concentrations of phenolic compounds in bio-oil, indicating that ash components catalyze the cracking of lignin. Especially calcium concertation was concluded to be most significant regarding the lignin cracking reactions (Stefanidis et al. 2015). Mourant et al. (2011) reported that the most significant changes in bio-oil sugar compositions occurred when AAEM content increased from 0 to 0.2 w-%. On the other hand, increased concentration of phenolic compounds followed linearly increasing AAEM content.

4.2 Yields and phase separation

In general, it has been shown that ash contents above 1 w-% in biomass results in decreased bio-oil yield during pyrolysis (Carpenter et al. 2014). De-ashed feedstocks have been reported to give better bio-oil yields in both thermal and in catalytic pyrolysis as well as resulting in lower water content of bio-oils (Fahmi et al. 2008, Hernando et al. 2017, Mourant et al. 2011). However, the yields and reductions in water content seem to increase exponentially when inorganic

concentration is reduced (Mourant et al. 2011, Oasmaa et al. 2015). Thus, removing the most persistent inorganic components to reach low ash concentrations may be the most crucial aspect regarding the yield maximization, although easily removable potassium seems to be catalytically the most active individual element (Patwardhan et al. 2009). Persistent AAEMs may have the most significant effect due to their strong binding and interactions. Other option is that their concentration with other inorganics is enough to reach the most significant catalytic effects and increasing AAEM concentration enhances catalytic activity only moderately (Mourant et al. 2011).

Phase separation of bio-oil is a common phenomenon during the aging of bio-oil and AAEMs have been speculated to accelerate the aging by catalyzing reactions during storage (Baldwin & Feik 2013). In the case of fresh bio-oils, phase separation is problem especially when high ash content biomasses are used as feedstock (Oasmaa et al. 2010). Bio-oil is complex mixture of various components and homogenous solution exists only when these components are in equilibrium. When this equilibrium is distracted, the homogeneity is lost and phases will separate. During aging, the main mechanism of phase separation is formation of high molecular mass components that are water-insoluble. In the case of ash induced phase separation, phase equilibrium of bio-oil is disturbed by the reduced organic liquid content and by the extra water formation by dehydration reactions catalyzed by inorganic components during pyrolysis (Oasmaa et al. 2015). Thus, yield of bio-oil is reduced by ash catalyzed oxygen removal and water formation as well as by enhanced char and gas formation (Fahmi et al. 2008, Oasmaa et al. 2015). The effect of ash to oil yield and risk of phase separation can be seen in the Figure 12.

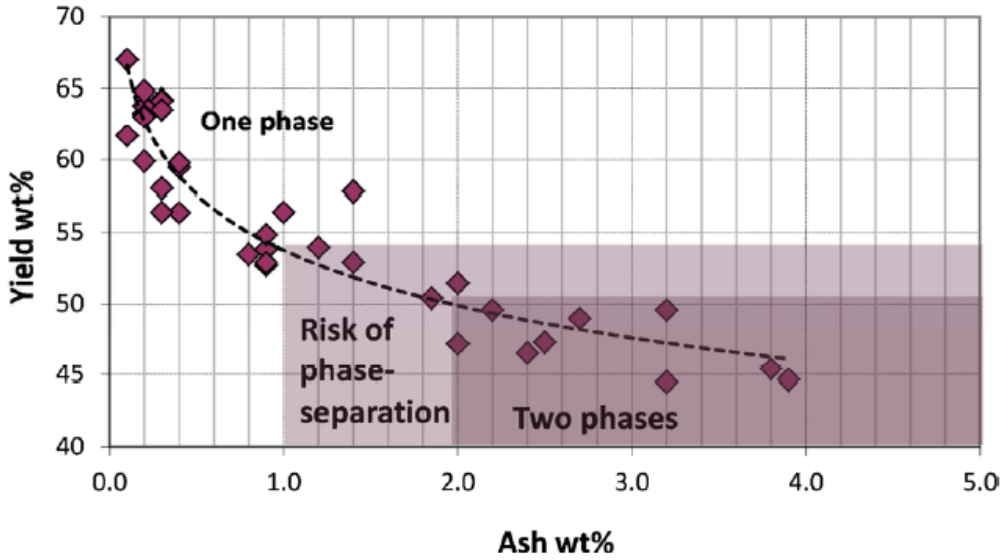

Figure 12. Yield of bio-oil as function of feedstock ash content and phase separation behavior (Oasmaa et al. 2015).

4.3 Inorganic transfer to bio-oil

Leijenhorst et al. (2016) reviewed and studied the transform of inorganics from biomass to fast pyrolysis oil. High ash feedstocks result typically in higher inorganic concentrations of bio-oil. However, over 95 % of inorganics present in biomass are typically not transferred into liquid product and are entrained in char. Thus, pyrolysis itself is efficient ash removal process.

Efficient and fast solid separation is the most important method to minimize the inorganics content in bio-oil (Leijenhorst et al. 2016). For example, efficient removal of aerosols and ash particles with hot-gas filtration instead of cyclone separation has been reported to reduce the inorganic content of bio-oil significantly, but with the expense of bio-oil yield (Baldwin & Fink 2013). However, differences exist in the behavior between the groups of inorganics and in their volatilization (Keown et al. 2008, Doshi et al. 2009, Leijenhorst et al. 2016). Especially water-soluble and easily removable inorganics are expected to be more reactive and susceptible to volatilization during heating (Baxter et al. 1998).

Leijenhorst et al. (2016) reported that all AAEMs were predominantly retained in char. However, in the case of alkali metals, significant amount was also transferred

to bio-oil. Alkaline earth metals ended up to much smaller extent into bio-oil and larger fraction was entrained in char particles. The average transfer degree of alkali metals was 8 % and with alkaline earth metals 2 %. Keown et al. (2008) obtained similar results and reported that alkali metals volatilize more easily during pyrolysis compared to alkaline earth metals.

With the alkali earth metals, concentration of metals in bio-oil has been shown to increase rather linearly with increasing metal content of feedstock (Leijenhorst et al. 2016). In the case of alkali metals, unlinear transfer has been detected. Leijenhorst et al. (2016) reported that larger fraction of alkalis was transferred to bio-oil when feedstock metal content was lower. However, authors postulated that reason for unlinearity might be equipment contamination by previous experiments. AAEM concentrations in bio-oil with changing feedstock metal content is presented in Figures 13 and 14.

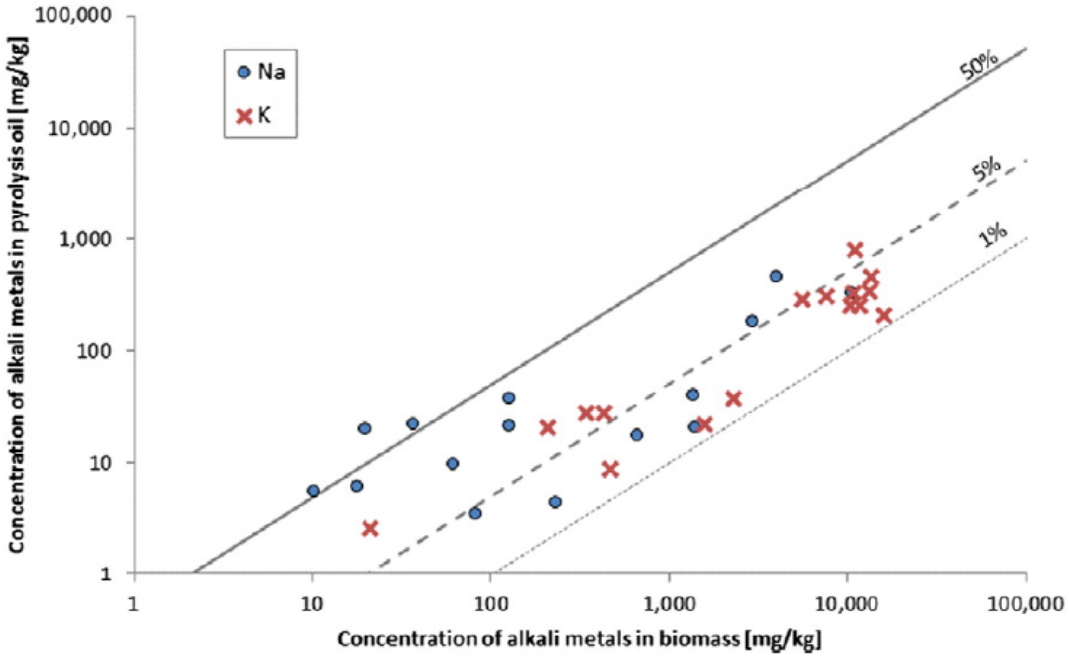

Figure 13. Concetrations of alkali metals in pyrolysis oil as function of feedstock metal content (Leijenhorst et al. 2016).

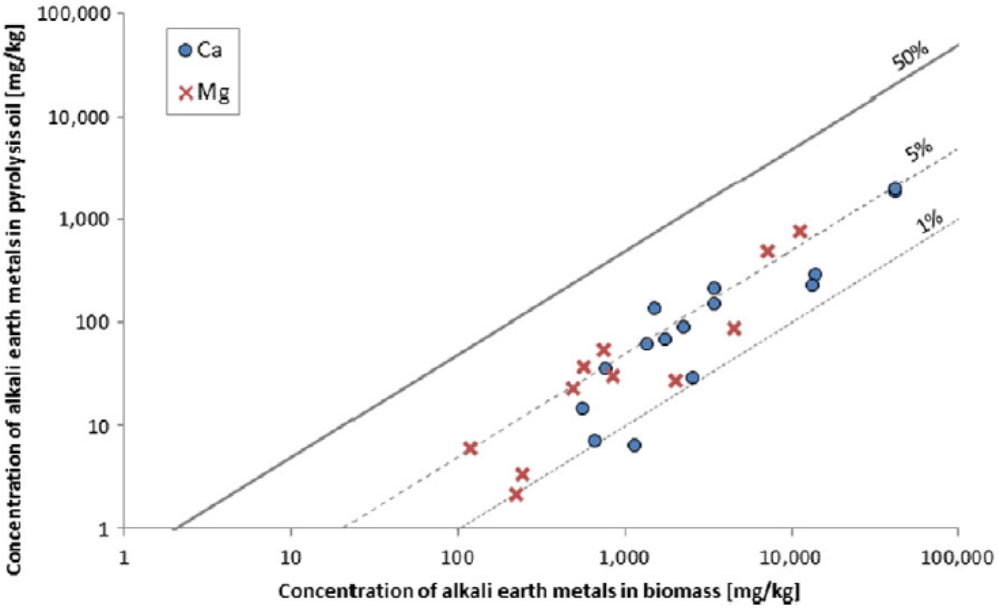

Figure 14. Concentrations of alkaline earth metals in pyrolysis oil as function of feedstock metal content (Leijenhorst et al. 2016).

Leijenhorst et al. (2016) suggested couple of reasons for different behavior of AAEM species. First, due to the reason that monovalent alkali metals are mainly present in their free ionic forms, they can react with volatile degradation products and transfer to bio-oil through volatilization of these components. In addition, calcium and magnesium are more often located inside the cell walls of plant and due to their divalent nature, two bond needs to be broken down to free these ions. Thus, alkaline earth metals are more likely to be bound on biomass through pyrolysis reactions and entrained in char particles. This may also lead to stronger binding to char particles compared to alkali metals. Alkali metals can be in more releasable form in char and can dissolve or transfer to bio-oil more easily if solids removal is poor. Direct volatilization and thermal ejection of inorganics is also possible transfer mechanism.

Sulfur was reported to react strongly with volatile components and was extensively transferred to bio-oil, but phosphor was largely retained in chars with transition metals and post-transition metals (Leijenhorst et al. 2016). Silicon is also reported to predominately accumulate in char fraction (Carpenter et al. 2014).

4.4 Catalyst deactivation in catalytic pyrolysis

Inorganics, especially AAEMs have been reported to accumulate on the acidic zeolite catalyst used in catalytic fast pyrolysis (Mullen & Boateng 2013, Paasikallio et al. 2014). Accumulation has related to the deactivation of the catalyst and accumulated inorganics, especially potassium, might change the behavior of the catalyst in reactions that it catalyzes (Mullen et al. 2017). Possible mechanism of deactivation is, that accumulated alkalis reduce the acidity of the catalyst, which result in hindered deoxygenation (Paasikallio et al. 2014) Potassium and iron has been reported to associate most strongly with zeolites and accumulate fastest on their surface (Mullen & Boateng 2013). Similar catalysts can also be used in upgrading of bio-oil and metals that end up in bio-oil can cause problems during further processing (Talmadge et al. 2014).

5 Separation of inorganics from biomass

Pretreatment of biomass prior to pyrolysis has awaken a lot of interest due to the many harmful effects caused by AAEMs during the pyrolysis process. In addition, pretreatment of biomass prior to combustion is extensively studied topic because AAEMs cause maintenance problems in power plants by slagging, fouling and corrosion (Davidsson et al. 2002). Liu et al. (2017) and Carpenter et al. (2014) have published comprehensive reviews regarding the pretreatment and its effects in thermochemical conversion processes. Although ash content can be controlled by harvesting time, significant amounts of inorganics will be present, especially in biomass waste fractions (Bridgwater 2018). Most commonly utilized pretreatment methods include simple mechanical separation, water washing and dilute acid washing. Washings are often done at or near room temperature, but higher washing temperatures have been studied. However, commercial scale processes for biomass washing prior to combustion have failed to be economically feasible.

5.1 Mechanical pretreatment

Sieving of biomass has been considered as a first pretreatment step. The ash content of grinded biomass has been reported to vary with the particle size,

concentration of ash being higher in fine particles than in coarser ones (Liu & Bi 2011, Miranda et al. 2012). Liu & Bi (2011) reported that in the case of switchgrass, over 20 % of ash was removed by separating particles smaller than 0.3 mm, which contributed 11 w-% to total weight of feedstock. Thus, simple mechanical sieving can be beneficial before other washing methods but is not sufficient alone. In addition, sieving will always lead to mass losses and generate waste fraction to be treated.

Mixing of feedstocks with different ash contents is also possible. Mixing can make the utilization of low quality feeds easier. Feedstocks can be formulated by mixing treated and untreated low and high ash feeds so that manageable ash levels are reached (Tumuluru et al. 2012). However, ash will still be concentrated in certain particles, which may result in different behavior and product distribution when compared with homogenous feeds.

5.2 Water washing

Results from several research groups have indicated that water washing is efficient way to remove majority of potassium, sodium and magnesium but removal of calcium is inefficient (Baxter et al. 1998, Davidsson et al. 2002, Jenkins et al. 1996, Mourant et al. 2011, Stefanidis et al. 2015). Water washing is considered to be more suitable for feedstocks with high ash content. In low ash content feedstocks, the proportion of inorganics bound strongly to organic structures of biomass is higher and these are not removable by water (Baxter et al. 1998, Fahmi et al. 2008). Water also fails in the removal of inorganics in ion exchangeable form (Scott et al. 2001). Results from several studies collected by Liu et al. (2017) indicate that although rather high removal rates for high ash feedstock are achieved, reaching of low levels of ash is challenging with water washing.

Water washing is typically done by filtrating water through the sample or soaking the sample in water bath. Using of de-ionized or distilled water is preferable due to the mineral content of municipal tap water. In addition, several parameters, such as agitation, washing time, water-to-biomass ratio, temperature and biomass

particle size may have effect on washing efficiency which partly explains varying results from literature (Morgan et al. 2017). Few reported results from water washing experiments are presented below.

Jenkins et al. (1996) washed wheat and rice straw in room temperature with large amounts of distilled water and tap water. Reported removal rates with distilled water were 90 % for potassium and 68 % for sodium and magnesium. In addition, 98 % of chloride, 55 % of sulfur and 72 % of phosphor were removed. Total ash content of wheat straw was reduced 68 %. However, the initial ash content of 13.4 w-% in wheat straw was rather high and the total ash content after washing was still 4.2 w-%. With tap water, 5.0 w-% of ash was left after washing. In the case of rice straw, only 10 % reduction in total ash content was achieved, although the initial ash content of straw was 19.6 w-% and majority of potassium and sodium were removed. Reason for this is probably the high structural mineral silica content in rice straws (Marschner 2011). These results indicate that reduction in total ash content may be poor indicator regarding the removal rate of alkalis, at least when feedstock with high ash content is considered.

Fahmi et al. (2008) soaked switchgrass in de-ionized water for 2 hours at room temperature with biomass to water ratio 1:10. Almost 90 % of alkali metals were removed but total AAEM removal rate was approximately 10 % due to persistency of calcium and magnesium. Total ash content was reduced from 4.3 w-% to 3.4 w-%. Davidsson et al. (2002) washed wheat straw and wood waste mixture consisting mainly from pine and birch with de-ionized water in room temperature with biomass to water ratios of 1:5 and 1:20. Larger amount of washing liquid did not offer any significant benefit. They reported potassium and sodium removal rates of 50 - 80 % for wheat straw and 35 % for wood waste. Total ash content reductions were on average 48 % for wheat straw and 36 % for wood waste.

Renkonen (2016) performed washing tests with tap water and forest residues. Temperature of washing water was 40 °C and biomass to water ratio 1:15. Ash content of forest residues was reduced by 24 % from 3.2 w-% to 2.4 w-%.

Mourant et al. (2011) soaked mallee wood in deionized water for 2, 24 and 48 hours in room temperature with biomass to water ratio 1:10. Washing efficiency increased with increasing washing time. Particle size of washed biomass was 180 - 425 µm. Potassium was almost completely removed but magnesium and especially calcium was more recalcitrant. However, water washing was capable to remove more than 70 % of AAEM species from the initial 0.7 w-% AAEM concentration. Unremoved part consisted mainly of calcium. Total ash reduction was not reported. Stefanidis et al. (2015) performed tests with beech wood in different temperatures and with varying washing times. They reported that increasing washing time enhanced only slightly total ash removal and most of the ash was removed during first 2 hours. On the other hand, washing at 50 °C was significantly more efficient than washing in room temperature. Ash reduction improved from 21 % obtained in room temperature to 43 % at 50 °C. However, the initial ash content of beech wood was only 0.68 w-% on dry mass basis, and thus, the absolute ash reductions and changes in the washing efficiencies were not large.

In addition, Stefanidis et al. (2015) performed water washing with different feedstocks grinded to fine particle size (90 - 500 µm). Washings were performed at 50 °C with 4 h residence time. Removal efficiencies were 43.1 % for pine residues, 29.8 % for eucalyptus, and 17.2 % and 43.2 % for wheat and barley straws, respectively. With all samples, 80 - 90 % of potassium and sodium, 30 - 60 % of magnesium and 5 - 30 % of calcium were removed but efficiencies varied between feedstocks. For example, calcium was the most persistent with eucalyptus and pine residues where removal efficiencies were below 10 %, while with wheat straw over 30 % of calcium was removed.

Liu et al. (2018) studied hot water extraction with switchgrass and pine bark. The temperature range studied was 60 - 140 °C with 15, 30 and 45 residence time. Increased temperature and treatment time gave better ash removal results but resulted also in larger mass losses. The potassium, sodium, magnesium and calcium removals were in the range of 94.9 – 98.8 %, 47.9 – 72.4 %, 58.7 – 83.5

and 8.5 – 13.0 %, respectively, for switchgrass. Pine bark was more challenging and lower metal removals were achieved. Corresponding removal efficiencies for pine bark were 50.8 – 67.5 %, 29.2 – 60.1 %, 9.7 – 50.8 % and 3.3 – 33.0 %, respectively.

5.3 Acid washing

Dilute acid washing of biomass has been reported to be efficient method to remove most of the AAEMs and to decrease the total ash content of biomass. 80 - 90 % of AAEMs in biomasses have been reported to be in water-soluble or in ion-exchangeable form, meaning that they are potentially removable by acid treatment (Baxter et al. 1998, Davidsson et al. 2002, Jenkins et al. 1996, Mourant et al. 2011, Scott et al. 2001). However, total ash reductions do not reach the same levels as AAEM content reductions, but results are significantly better than with water washing (Liu et al. 2017).

Acids tested in washing experiments include dilute solutions of sulfuric acid, hydrochloric acid, acetic acid, hydrofluoric acid and nitric acid (Liu et al. 2017). Dilute nitric acid solutions are perhaps the most potential ones because they do not cause severe mass losses and are efficient in ash removal (Stefanidis et al. 2015). One problem with acid washing is that acids often consist of elements that are aimed to be removed from biomass. In addition, acid washing generates waste streams that need to be neutralized (Renkonen 2016) and causes mass losses through acid catalyzed hydrolysis reactions of polysaccharides (Pedersen & Meyer 2010). Reduction in degree of polymerization of lignocellulosic components may also change their behavior and degradation during pyrolysis. In addition, mineral acids used in washing need often to be washed or rinsed away with extra amount of water. Some results from acid washing of biomass are presented below.

Mourant et al. (2011) soaked mallee wood in 0.1 % nitric acid solution for two hours. Temperature was 25 °C and biomass to liquid ratio 1:10. Complete removal of potassium, sodium and magnesium were achieved and removal efficiency of

calcium was 96 %. Results from acid washing compared to water washing are presented in Figure 15. Total ash reduction was not reported.

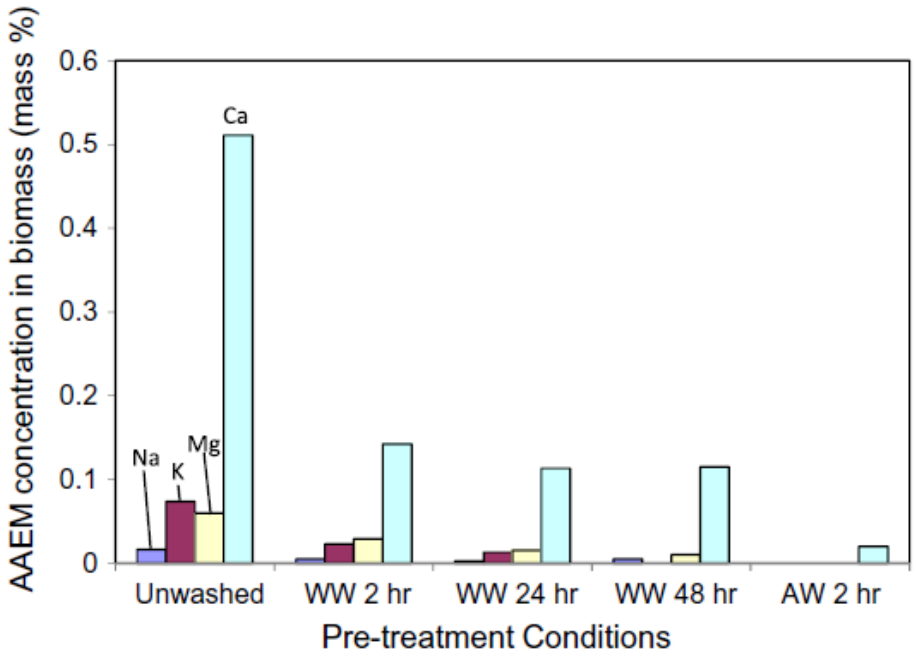

Figure 15. AAEM concentration in differently pretreated mallee wood on dry mass basis. Abbreviations WW and AW stands for water and acid washing, respectively (Mourant et al. 2011).

Stefanidis et al. (2015) studied nitric and acetic acid washing of forest residues, agricultural waste and eucalyptus with varying temperatures, washing times and acid concentrations. Nitric acid was found to be more efficient than acetic acid and washing time improved ash removal only slightly. Higher acid concentration improved ash removal but improvements were only moderate. Washing at 50 °C was significantly more efficient than washing at room temperature. Proportionally ash removal was most successful with forest residues, but it had the lowest initial ash content. With 1 % nitric acid solutions and residence time of 2 hours at 50 °C achieved ash removal efficiencies were 87.3 % for pine residues, 69.9 % for eucalyptus, and 21.8 % and 54.0 % for wheat and barley straws, respectively. AAEM removal rates were close to 100 % with both tested acids. However, calcium of eucalyptus was more recalcitrant than in other raw materials and removal efficiency stayed below 80 %.

In addition to conventional acid washing, acidic condensate from pyrolysis process has been studied as a washing liquid. Oudenhoven et al. (2013) managed to remove 96 % of ash from pine wood by soaking it in acidic condensate for 2 hours in 90 °C with biomass to liquid ratio 1:10. The condensate included 9.5 w-% acetic acid, 7.6 w-% acetol, 1.4 w% propionic acid, 1.7 w-% guaiacol, 19.5 w-% of other organics and 60.5 w-% of water. Renkonen (2016) tried also washing of forest residues with acidic condensate at 40 °C and was able to remove roughly 40 % of ash. However, the removal efficiency was not high enough for the process to be economically feasible. In addition, the amount of condensate produced in the process is small compared to the amount of biomass processed and the condensate includes toxic, corrosive and flammable components. Thus, processing of waste waters would be costlier if condensate would be extensively used.

5.4 Other washing methods

In addition to water and acid washing, washing with bases have been studied. Kazi et al. (1998) reported 86 % reduction in ash content of barley straw with the companied removal of extractives when they impregnated straws with 10 w-% NaOH solution. However, base washing results often in high mass losses and reductions in degree of polymerization of lignocellulosic macromolecules. Waste streams generated need to be neutralized and introducing large amounts of ions into biomass is not beneficial when AAEMs are aimed to be removed.

Recent study by Edmunds et al. (2017) introduced the utilization of chelating agents in removal of metals from lignocellulosic feedstocks. Chelating agents studied were industrially available citric acid (CA) and ethylene-di-amine-tetra-acetic acid (EDTA). EDTA is widely used also in pulp industry to remove metals from pulp prior to hydrogen peroxide bleaching. Conventionally chelating agents are used in the presence of acids, because acids are capable to release the ions trapped in ion-exchangeable form (Brelid et al. 1998, Chirat et al. 2011).

Experiments by Edmunds et al. (2017) were conducted in microwave digester with washing times of 5, 10, 15 and 20 minutes and biomass to solvent ratio of 1:20. Concertation of EDTA and CA were 10 g /L. CA solution was strongly acidic but EDTA formed neutral or slightly basic solutions with water. However, the environment during the experiments was acidic due to the conditions used. Temperature and pressure increased during experiments and reaction was microwave assisted. Thus, results are not comparable with previously introduced results, but performance of CA and EDTA can be compared to performance of water within the study. In the experiments, EDTA outperformed water in total ash removal, but CA was only slightly more efficient. Removal efficiency of EDTA increased with increasing treatment time. With reaction time of 20 minutes and final temperature and pressure of 128 °C and 6.3 bars, total ash reduction was 87.3 %, while with 5 min reaction time and final conditions of 65 °C and 4.0 bars ash reduction was approximately 60 %. With water, the pressures were the same but final temperature were 62 °C and 109 °C for 5 and 20 minute reaction times, respectively. However, ash removal stayed on the same level between the runs and was approximately 45 %. Especially calcium, magnesium and silicon removal enhanced with EDTA washing compared to water washing. Potassium removal was a bit better in pure water with over 99 % removal compared to 97 % achieved with EDTA. Mass losses were at same level with water, CA and EDTA (Edmunds et al. 2017).

A disadvantage of EDTA is its high price compared to mineral acids. In addition, EDTA may need acidic conditions to work efficiently, it is challenging to recycle and it is biologically persistent (Brelid et al. 1998, Edmunds et al. 2017). However, biodegradable chelating agents, such as nitrilo-tri-acetic acid (NTA) can potentially solve this problem (Edmunds et al. 2017).

5.4 Thermal pretreatment

In addition to washing pretreatments, more severe methods for biomass pretreatment prior to pyrolysis have been considered. These methods include,

steam explosion, hydrothermal carbonization and torrefaction (Liu et al. 2017, Carpenter et al. 2014). However, reported ash removal efficiencies are not exceptionally better compared to conventional washing methods (Liu et al. 2017). In addition, these pretreatments lead to major changes in feedstock structure and composition, and their behavior during pyrolysis. This will also change the process concept significantly. In addition, thermal treatments are energy intensive and high temperatures and pressures increase the equipment costs and process complexity. Thus, these methods are out of the scope of this thesis.

5.5 Conclusions and challenges of washing methods

AAEMs are to large extent removable with water, when sufficient temperatures, washing times and amounts of water are used. Potassium and sodium concentrations are reduced to minimum from the initial levels and large portion of magnesium is typically removed, but significant amounts of calcium will be left in biomass. In addition, total ash removal efficiencies vary a lot, but typical values are in the range of 10 - 50 %. When acids are utilized, removal efficiencies and rates are enhanced. Lower AAEM concentrations are reached with shorter retention times. Especially calcium removal is enhanced and almost complete AAEM removals are reported. Total ash removals are improved although reported results, again, vary a lot. Typical range for results is 30 - 90 %. In addition, bases and chelating agents as well as thermal pretreatment methods are studied.

In general, washing is more efficient with high ash feedstocks and efficiency of inorganics removal is improved when processing severity increases. However, increasing temperatures and acid concentration will lead to increased mass losses (Liu et al. 2017). This reduces bio-oil yield and may affect to its quality due to the chemical changes in the feedstock. In addition, rinsing of biomass after acid washing may be necessary so that the pyrolysis process is not disrupted. Although, small traces of acid left in biomass can even improve the yield of certain components in pyrolysis, extensive acid traces left in biomass can reduce the yields of sugars and some other species (Pecha et al. 2015). However, more information

regarding this aspect is needed. One challenge is also that acidic waste liquids needs to be neutralized. In the end, the feasibility of washing is dependent from the increased bio-oil yield and improvements in its quality.

Inorganics are not the only chemical species extracted from biomass by these washing methods. For example, water-soluble phenolic compounds and non-cellulosic sugars can be extracted from wood bark with hot water (Kemppainen et al. 2014, Dou et al. 2018). Water-soluble compounds include also minor amounts of species such as proteins, starch, pectins and some other carbohydrate derivatives (Sjöström 1981). Feed with high extractive content, such as bark, can possibly result in utilizable extractive concentration in washing liquids, but also increase the organic loading of wastewaters. Solubility of these components varies also by conditions used. For example, solubility of phenolic compounds from pine bark increases when pH increases and thus more of these species will be dissolved in neutral than in acidic conditions (Alakurtti 2018).

Largest disadvantages of washing methods is the wetting of the biomass particles. Drying of biomass after washing is necessary because the moisture content of pyrolysis feed should not exceed 10 w-% (Birdgwater 2018). Conventionally biomass is milled to suitable particle size after it is dried. Grinding and subsequent sieving are easier and more efficient with drier feedstock. Grinding needs more energy with wet particles and wet particles have stronger tendency to aggregate and block the sieves (Mani et al. 2004). On the other hand, washing would be beneficial to do with smaller particles to enhance the inorganics removal. Substantially larger particles than the 5 mm used in fast pyrolysis would most probably have degenerative effects on washing efficiency due to the increased mass transfer limitations (Turn et al. 1997). However, drying of feedstock twice (before grinding and after washing) would decrease the economic feasibility of the process. If drying is wanted to be minimized, either washing of larger particles or grinding of moist feedstock is unavoidable.

6 Conclusions for literature part

The most abundant inorganic constituents of lignocellulosic feedstocks are alkali and alkaline earth metals potassium, sodium, magnesium and calcium, transition metals iron and aluminum, metalloid silicon and non-metals phosphorous and sulfur. In addition to these, several other metals are present in lesser quantities. From the perspective of fast pyrolysis, these ash-forming elements act as impurities due to their harmful effects during processing.

Inorganic content of biomass, predominately AAEMs, catalyze water, char and gas formation and reduce the bio-oil yield. Altered degradation pathways, catalyzed by metals, also affect chemical composition of bio-oil. Especially sugar concentration of bio-oil is reduced and fraction of high molecular mass lignin increases when lignin is cracked less to phenolic compounds. In addition, removal of inorganics from biomass can reduce the inorganic content of bio-oil. Metals in bio-oil can cause catalyst poisoning during further upgrading and accelerate the aging of bio-oil during storage.

Inorganics are present in biomass as water-soluble ions, salt precipitates, minerals, in ion-exchangeable form and some are bound covalently to organic molecules. Large portion of alkali metals are removable with water. Alkali earth metals are more resistant to water washing, calcium being more persistent than magnesium. Acid washing is more efficient regarding the total inorganics removal, because acids are capable to remove also the inorganics in ion-exchangeable form and acid soluble precipitates and minerals. Especially calcium, but also magnesium removal is enhanced. With both washing methods, increased severity of treatment conditions has been reported to improve the washing efficiency. In general, washings are considered to be more efficient with high ash content feedstocks. However, efficiencies of washing methods vary with different feedstocks since the ash and biomass compositions change with botanical source.

From the perspective of yield maximization and minimizing the changes in chemical composition of bio-oil, reaching of low ash levels is the most essential

aspect in biomass pretreatment. Ash levels above 1 w-% on dry mass basis are reported to result in higher water content and reduced bio-oil yields. Especially the most persistent AAEMs and inorganics have been shown to have the significant effect on yield, although the easily removable potassium is considered to be catalytically the most active. AAEM levels already below 0.2 w-% has been reported to give major changes in chemical composition of bio-oil with washed raw materials. This might be due to the strong interactions of persistent elements with organic matter or that already small concentration possesses the most of the catalytic activity and when concentration is increased, only moderate enhancement in activity is obtained.

When the metal content of produced bio-oil is considered, benefits from reduced inorganic content are more linear. Reduced ash content of feed result in lower metal content of bio-oil, especially in the case of alkali metals. The water-soluble and easily removable part of inorganics is the most susceptible to end up in bio-oil, while strongly bound inorganics are more probably entrained in char. Thus, washing only the easily releasable inorganics with water might be beneficial when metal content of oil is aimed to be minimized and further upgrading of bio-oil is considered.

However, acid washing is always more efficient in total reduction of inorganics. Larger ash reductions give larger improvements in yields and reduce the inorganics content of bio-oil more. In addition, removal of inorganics is faster with acids. On the other hand, utilization of water minimizes the use of chemicals, which might enhance the process economics and make it more sustainable from environmental perspective. In addition, washing water treatment and construction of closed water system are easier if water could be used as washing liquid. Although previous studies have indicated that washing of pyrolysis feeds is hardly economically feasible, novel usages of bio-oil and decreasing feedstock qualities may lead to situation where feedstock pretreatment is beneficial, if not necessary.

EXPERIMENTAL PART

7 Introduction for experimental part

In the experimental part, leaching efficiency of water and aqueous acid in removal of ash and AAEMs from different biomass feedstocks (straw, eucalyptus and forest residues) was studied with the aim of clarifying their potential as a pretreatment for industrial bio-oil production. The experimental section consisted of two parts: laboratory scale and bench scale washing experiments.

8 Washing experiments

The initial plan of the washing experiments was to study the effect of various parameters on efficiency of water washing in removal of AAEMs. However, the acid washing was also studied due to the poor total ash reduction of water washing. The most important parameters for water washing recognized from literature were the amount of washing liquid, washing temperature and washing time. In addition, parameters such as the amount of rinsing water, washing efficiency of tap water, and particle size distribution of raw material can have effects. Experimental plan for water washings is presented in Table 4.

Two major reason raised interest towards studying the water washing. First reason was the chemical costs and weak economic feasibility of acid washing (Renkonen 2016). The second reason was the high water solubility of potassium, sodium and to some extent magnesium, although the calcium is poorly removed with water (Baxter et al. 1998, Davidsson et al. 2002, Jenkins et al. 1996, Mourant et al. 2011). AAEMs are the most catalytically active ash components and especially monovalent potassium and sodium, are susceptible to transfer into the bio-oil during fast pyrolysis. Thus, removing of them may be beneficial when metal content of bio-oil and further upgrading of it is considered (Leijenhorst et al 2016). Although the main goal was the removal of AAEMs, maximizing the reduction of total ash was also considered.

Table 4. Experimental plan for water washing tests. T, t and B:W stands for temperature, washing time and biomass to washing liquid ratio, respectively.

Water washing experiments				
Changing parameter	T (°C)	Washing water (B:W)	t (min)	Rinsing water (B:W)
Amount of washing water	20	1:5	120	1:50
	20	1:10	120	1:50
	20	1:20	120	1:50
Temperature	20	1:5	120	1:50
	50	1:5	120	1:50
	80	1:5	120	1:50
	20	1:10	120	1:50
	50	1:10	120	1:50
	80	1:10	120	1:50
Washing time	50	1:10	0	1:50
	50	1:10	120	1:50
	50	1:10	240	1:50

In the case of acid washing, the most important variables recognized were the used acid, the washing temperature, acid concentration and washing time. Typically, shorter residence times are needed in acid washing compared to water washing. Nitric acid is one of the most utilized acids in washing due to its efficiency compared to other organic and inorganic acids, its gentleness towards macromolecules of biomass and the high solubility of AAEM nitrate salts (Carpenter et al. 2014, Liu et al. 2017). In addition, traces of nitrates left in biomass are less harmful compared to e.g. chlorine in hydrochloric acid, which is susceptible to transfer in bio-oil and can cause corrosion problems and catalyst deactivation during further upgrading (Davidsson et al. 2002, Leijenhorst et al. 2016). Thus, nitric acid was chosen as acid in acid washing experiments. Parameters investigated were temperature, washing time and acid concentration. In addition, the efficiency of tap water was tested with each raw material. Experimental plan for acid washing tests can be seen in the Table 5. The sufficient amount of rinsing water to wash away the acid traces is also important parameter in large scale applications, but its optimization was excluded from this thesis.

Table 5. Experimental plan for acid washing tests. T, t and B:W stands for temperature, washing time and biomass to washing liquid ratio, respectively.

Nitric acid washing experiments					
Changing parameter	T (°C)	Washing liquid (B:W)	t (min)	Acid concentration	Rinsing water (B:W)
Temperature	20	1:10	120	1 %	1:50
	50	1:10	120	1 %	1:50
Washing time	50	1:10	30	1 %	1:50
	50	1:10	120	1 %	1:50
Acid concentration	50	1:10	30	0.1 %	1:50
	50	1:10	30	0.5 %	1:50
	50	1:10	30	1 %	1:50
Amount of washing liquid	50	1:5	30	1 %	1:50

8.1 Raw materials

Raw materials washed in this thesis were pine forests residues, eucalyptus and wheat straw. All raw materials were provided as dried to moisture content of 6 - 10 w-%. Raw materials were grinded and sieved to particle size 0.55 - 0.98 mm. Forest residues and straw were treated at VTT, but eucalyptus was grinded and sieved by the supplier of the raw material. Deionized water (DI) was used as washing liquid in water washing experiments, but in acid washings, also tap water was tested. Acidic washing liquids were diluted from 65 w-% nitric acid. Raw materials were stored in cold in between the experimets.

8.2 Washing setup in laboratory experiments

Laboratory washings were carried out in sealed glass bottles. Bottle caps had holes so that the temperature of the suspension could be followed with thermometer and that the pressure in the bottles would not rise extensively during heating. Heating of the samples was provided with oil bath to keep the temperature as steady as possible. Oil bath was heated with plate heater equipped with magnet stirrer. Experimental procedure is described below.

Biomass and preheated washing liquid was weighted in the bottle and stirring was started immediately after addition of liquid. In room temperature tests, timing

was started when the stirring was turned on. In heated experiments, timing was started when the aimed temperature was reached. With 50 °C tests, temperature was easily manageable and timing could be started immediately after the start of stirring. In 80 °C tests, controlling of the initial temperature was more challenging although the glass bottles and washing water was preheated. In these tests, sufficient temperatures were reached 10 - 15 minutes after the start of stirring. Temperature varied within ± 2.5 °C from the aimed temperature during the runs. After the residence time was reached, the stirring was stopped and the sample was filtered with a Buchner funnel. Rinsing water temperature was the same as during the washing. Samples were taken from the washing and rinsing water. Washed biomass sample was collected, weighted and its moisture content was analyzed. Solid samples were dried at 80 °C over night for further analyses. To ensure the washing results and to minimize the possible heterogeneity of solid samples, tests were carried out as duplicates under each conditions.

8.3 Washing setup in bench scale experiments

Bench scale washing experiments were performed in cylinder shaped and Teflon-coated vessel equipped with heating jacket and mixer. Volume of the vessel was 100 liters. Washing conditions for bench scale tests were chosen based on the results from laboratory experiments. Washing liquid was measured in liters and was heated in the vessel. When the correct temperature was reached, five kilograms of raw material was weighted into the vessel. Timing was started after the addition of raw material. The suspension was mixed and temperature of the suspension was followed during the runs. After the residence time was reached, the suspension was drained from the valve located in the bottom of the vessel. Then, the suspension was filtered through sieve and filtered solids were rinsed with 50 liters of de-ionized water. After rinsing, biomass was dried overnight in the oven at 50 °C to reach the aimed 5 - 10 % moisture content.

8.4 Analyses

Ash and moisture content of solid samples were determined by thermogravimetric analysis according to standard SFS-EN ISO 18122. The equipment used was LECO

Corporation TGA-601 Thermo Gravimetric Analyzer. Moisture content of raw materials was followed daily with Adam PMB Moisture Analyzer. Total organic carbon was measured from washing waters with Shimadzu TOC-5000A Total Organic Carbon Analyzer. Elemental analyses of inorganics in biomass were conducted by dissolving samples in nitric acid (65 %) and determining the metal contents from the solutions. Approximately 500 mg of sample was weighted in Teflon-containers with the acid and heated in a microwave oven for one hour at 200 °C. Samples were cooled and diluted with MQ-water. Potassium and sodium contents were determined with Varian 240 AA atomic absorption spectrometer. Ca, Mg, Si, Fe, Al, P and S were measured with Perkin Elmer DV 7100 ICP-OES Spectrometer.

8.5 Results and discussion

Discussion and presentation of result is divided into four parts: analyses and characterization of raw materials, results from water washing experiments in laboratory scale, results from acid washing experiments in laboratory scale and bench scale washing experiments. Due to the large amount of data not all results are presented within the text. However, the complete set of the results can be found from appendices. Particle size distribution of raw materials and ash content of fractions are presented in Appendix 1, ash content determination by thermogravimetric analyses in Appendix 2, results from elemental analyses of treated and untreated biomasses in Appendix 3 and results from total organic carbon analyses of washing liquids in Appendix 4.

8.5.1 Raw material analyses

Particle size distribution of raw materials and ash content of obtained fractions was examined. Small differences existed in the particle size distribution. The size distribution of eucalyptus particles was a bit wider and a significant portion stayed on the 1 mm sieve. Otherwise, the distributions were similar. In the case of forest residues and eucalyptus, no differences in ash content of differently sized particles were observed. However, with wheat straw, ash content increased significantly

with decreasing particle size. Similar results have been presented with rice straw (Jenkins et al. 1996). Particle size distributions and ash content of fractions of wheat straw are presented in the Figure 16.

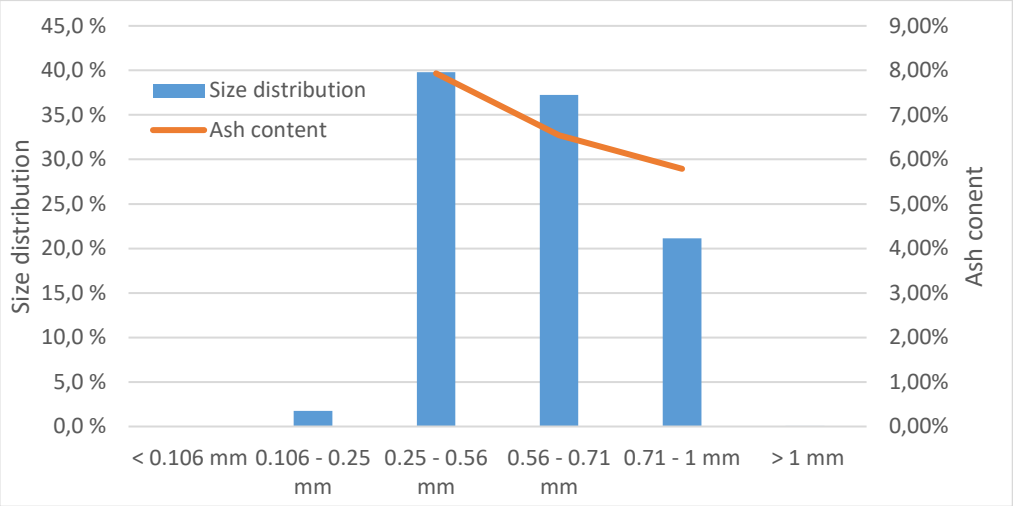

Figure 16. Particle size distribution of wheat straw and ash content of fractions.

Concentrations of K, Na, Ca, Mg, Si, Fe, Al, P and S and ash content of raw materials can be seen in Table 6. Potassium, calcium, magnesium and silicon were abundant in all raw materials. Sodium was present in the wood biomasses, but sodium content of straw was low. However, significant differences in the concentrations of these elements existed. Calcium content in eucalyptus and potassium content in wheat straw were much higher compared to other raw materials. Eucalyptus contained rather large amounts of iron and aluminum. In addition, high silicon content was observed especially in wheat straw but also in eucalyptus. Silicon content of wheat straw was expected but typically, such high silicon concentrations are not observed in wood biomass (Wilén et al. 1996). Thus, high silicon content of eucalyptus may be indication of contamination of sample by soil. Moisture content of the raw materials varied slightly. Moisture contents were 6.3, 7.1 and 9.1 w-% for forest residues, eucalyptus and wheat straw, respectively.

Table 6. Ash content (%) and concentrations (ppm) of certain ash forming elements in untreated raw materials on dry mass basis.

Raw material	K	Na	Ca	Mg	Si	Fe	Al	P	S	Ash
Forest residues	700	200	1300	200	800	200	200	< 200	200	0.74 %
Eucalyptus	2600	500	7500	900	6000	800	1200	< 200	400	4.75 %
Wheat straw	7600	< 50	1700	700	17000	< 200	400	< 200	400	6.91 %

Fraction of AAEMs from the measured inorganics was the highest in forest residues largely due to its low silicon content. With eucalyptus, the fraction of AAEMs was also rather high due to the high calcium content. With wheat straw, fraction of AAEMs was the lowest mainly due to the extremely high silicon content.

Total ash of forest residues was low and at the level that was more common for the stem wood (Wilén et al. 1996). On the other hand, ash content of the eucalyptus was higher compared to common values presented in literature (Stefandis et al. 2015, Morgan et al. 2016). Ash content of wheat straw was well in line with the values from the literature (Wilén et al. 1996, Stefanidis et al. 2015).

8.5.2 Water washing experiments

Tested parameters in water washings were the amount of washing liquid, temperature and washing time. Surprisingly, no large improvements in total ash removal were seen through changing of any parameters. First tested parameter was the amount of washing liquid.

Major effect of increased amount of washing water was more even and efficient mixing. Enhanced mixing was observed especially in the case of wheat straw and forest residues. With eucalyptus, observed improvements were the mildest and samples were mixed better with low amounts of water compared to other two raw materials. Forest residues absorbed more water compared to eucalyptus and formed suspension that was more viscous. Straw was less dense and occupied

larger space and thus larger water dose was needed. In fact, biomass to water ratio 1:5 could not be used with straw because suspension was only partly mixed.

Despite the enhanced mixing, the total ash content was not reduced significantly with the added water. In addition, no significant improvements in reduction of AAEM content with increasing amount of water were observed. AAEM contents of treated raw materials can be seen in Figures 17, 18 and 19. In addition, based on the TOC results, no more organic matter was dissolved in washing liquids, with larger amounts of washing water. Davidsson et al. (2002) reported similar results on the effect of the increased amount of washing water on total ash removal.

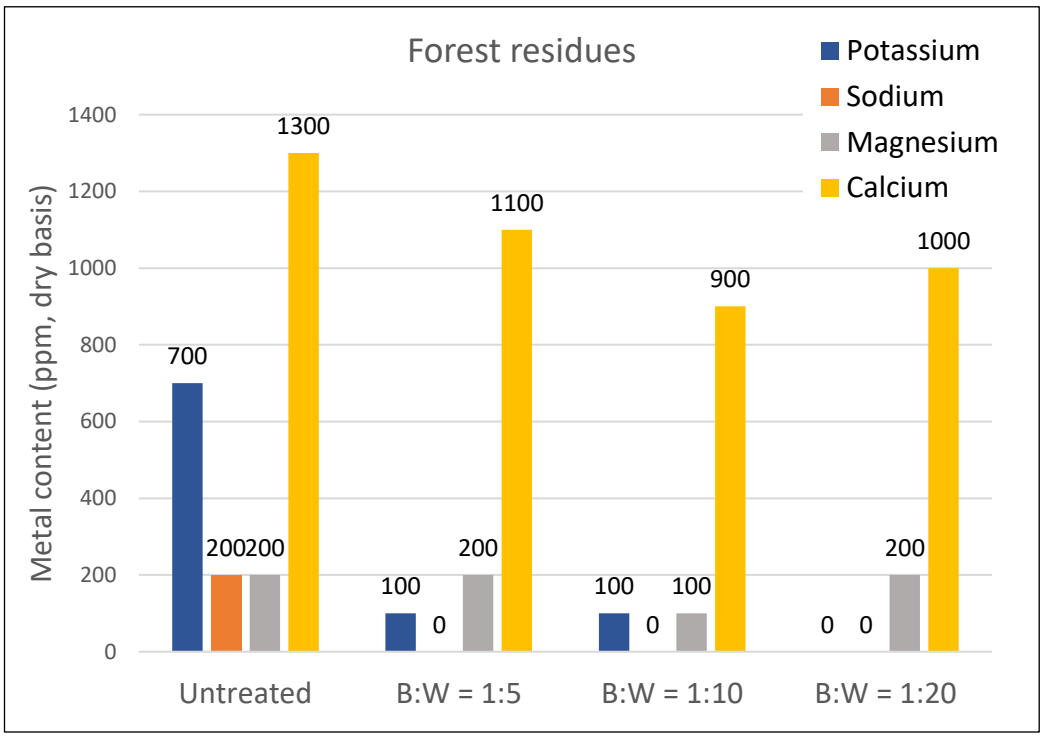

Figure 17. Alkali and alkaline earth metal content of forest residues before and after washing with biomass to water ratios of 1:5, 1:10 and 1:20 at room temperature.

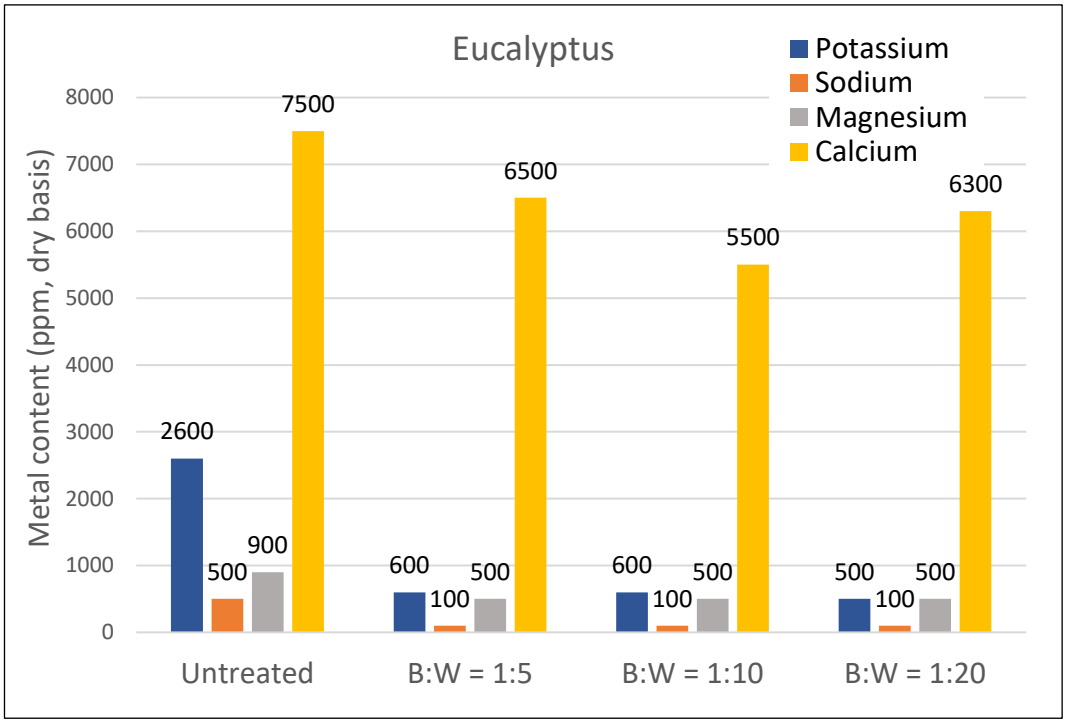

Figure 18. Alkali and alkaline earth metal content of eucalyptus before and after washing with biomass to water ratios of 1:5, 1:10 and 1:20 at room temperature.

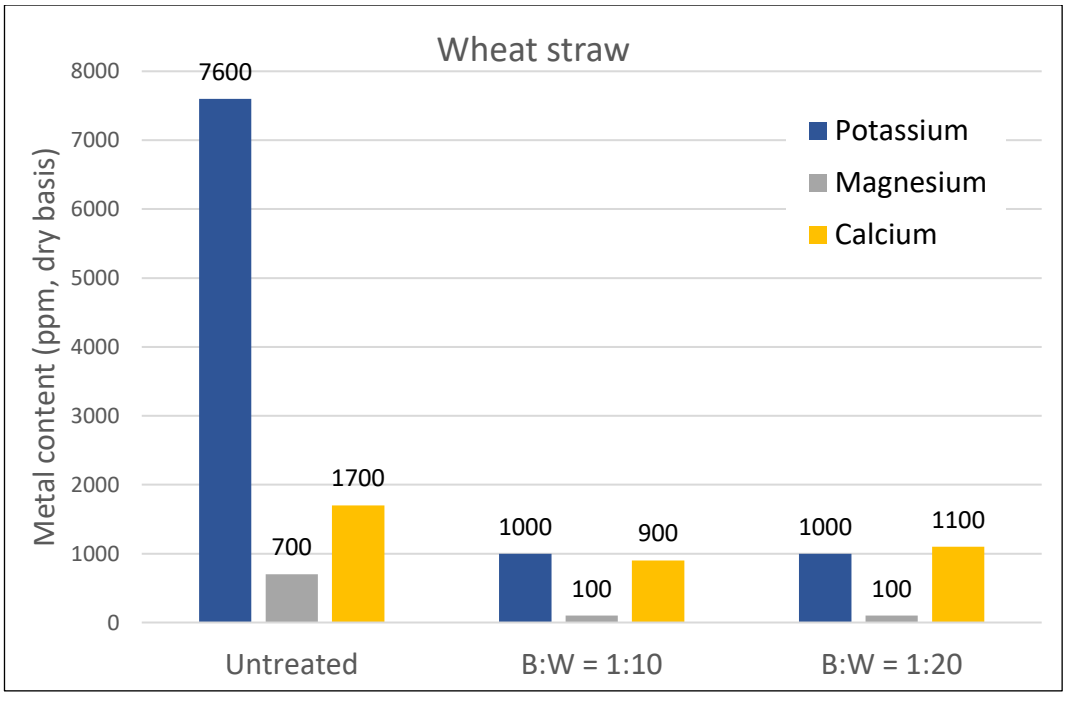

Figure 19. Alkali and alkaline earth metal content of wheat straw before and after washing with biomass to water ratios of 1:10 and 1:20 at room temperature.

In contrast to the results published by other authors (Stefanidis et al. 2015), increased washing temperature did not reduce the total ash content of samples significantly more with any raw material in our experiments. Clearest improvement was seen with the wheat straw, where 80 °C was slightly more efficient than lower temperatures.

Although reductions in total ash were hardly noticeable, reductions in concentrations of AAEMs were observed with increasing washing temperature. Especially calcium removal was more efficient at elevated temperatures with wood biomasses. However, changes were still small and for that reason, no significant improvements were observed with TGA. In the case of wheat straw, no large changes were observed even in the AAEM contents when temperature was varied which indicates that the increased ash removal efficiency in 80 °C was mainly due to the removal of other inorganics than AAEMs. AAEM contents of treated raw materials at different temperatures can be seen in Figures 20, 21 and 22.

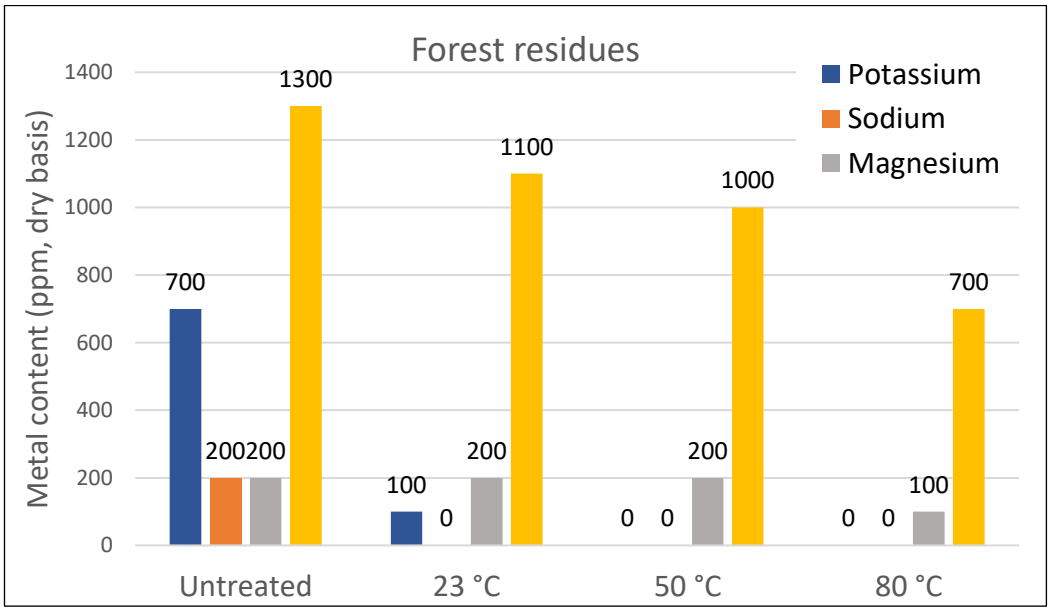

Figure 20. Alkali and alkaline earth metal content of forest residues before and after washing with washing temperatures of 23 °C, 50 °C and 80 °C with biomass to water ratio of 1:5.

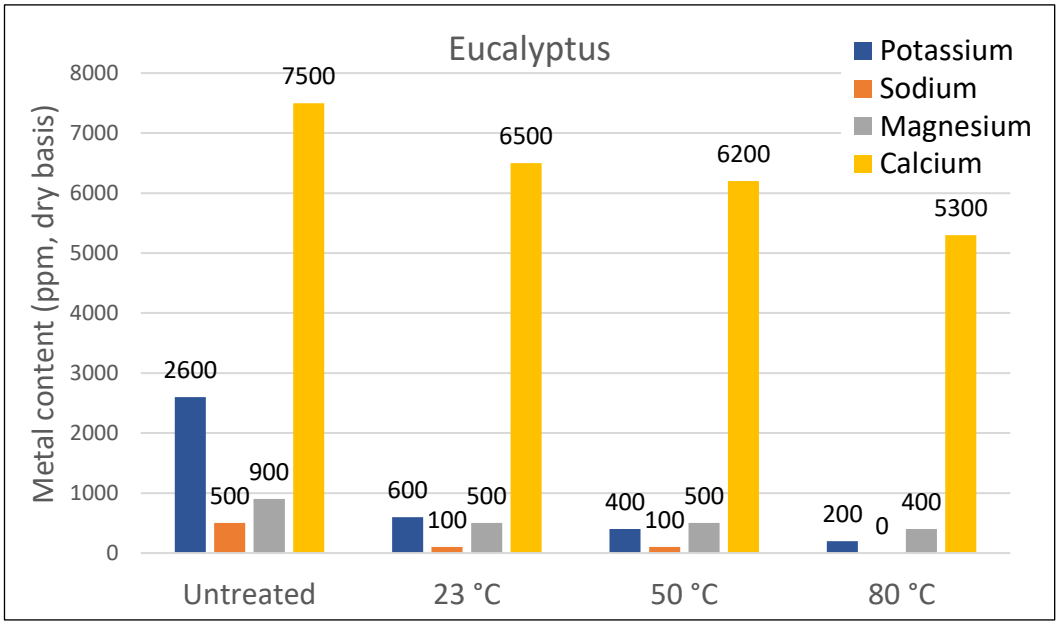

Figure 21. Alkali and alkaline earth metal content of eucalyptus before and after washing with washing temperatures of 23 °C, 50 °C and 80 °C with biomass to water ratio of 1:5.

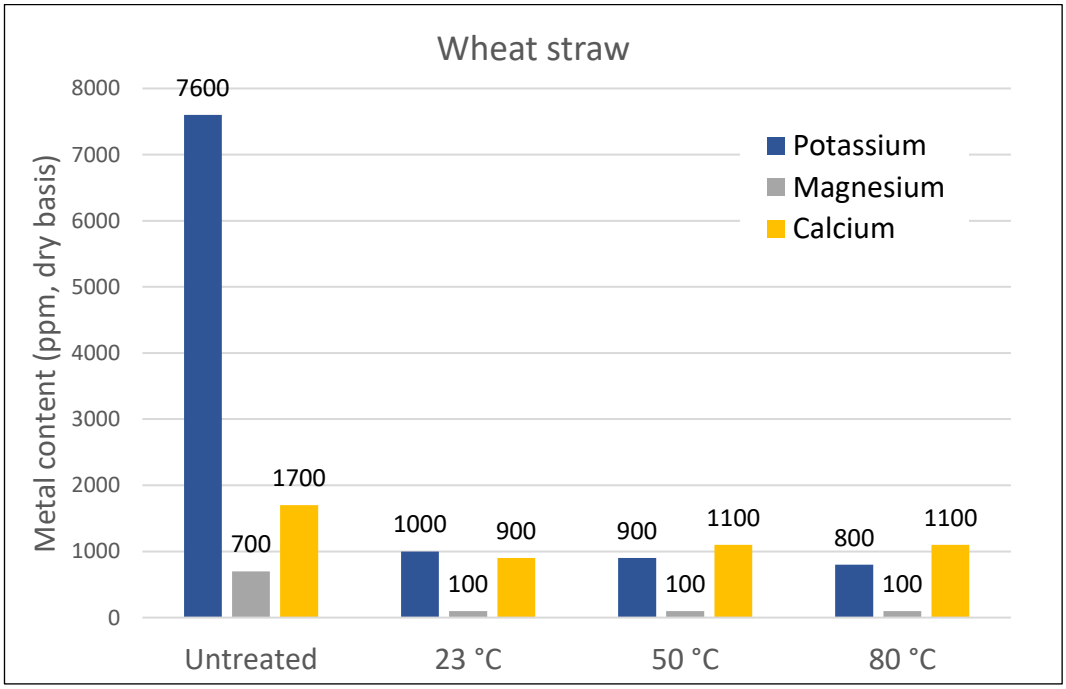

Figure 22. Alkali and alkaline earth metal content of wheat straw before and after washing with washing temperatures of 23 °C, 50 °C and 80 °C with biomass to water ratio of 1:10.

In addition, the total organic carbon content of the washing waters increased with increasing washing temperature. Although TOC varied a lot between the raw materials, the trends were similar (Appendix 4). The different TOC levels can be due to the differences in the water-soluble extractive content between the biomasses. For example, tropical species have typically higher extractives content than the woods in temperate climates. On the other hand, straws have higher hemicellulose content compared to woody biomasses (Willför et al. 2011), which can increase the dissolved sugar content if cells are broken down and hemicelluloses dissolved or degraded during washing.

Increased washing time improved the efficiency of washing slightly. Regarding the reduction in total ash content, best washing results were obtained with washing time of 240 minutes at 50 °C with forest residues and eucalyptus. With straw, longer washing time worked also well, but 120 min treatment time at 80 °C was as efficient. On the other hand, no significant reductions in AAEM contents were observed with washing time of 240 min compared to 120 min. In the case of straw, surprisingly large amount of AAEMs were removed already with the rinsing (0 min washing), which indicated that mass transfer limitations are less severe with straw. Low AAEM levels were reached also with the rinsing of forest residues, but absolute reductions were not as large due to the lower initial AAEM concentrations. Unfortunately, calcium and magnesium contents of 0 and 120 min washings with eucalyptus were unreasonably low and were probably subject to measurement errors. However, results obtained in 240 min test were not exceptionally better than results presented previously: calcium reduction was at the same level as at 80 °C test with 120 min washing time. In addition, slight increase in TOC of washing waters was observed with increasing washing time. Similar results from the effect of washing time to total ash removal have been published in the literature (Stefandis et al. 2015). AAEM contents of treated raw materials with different washing times can be seen in Figures 23, 24 and 25.

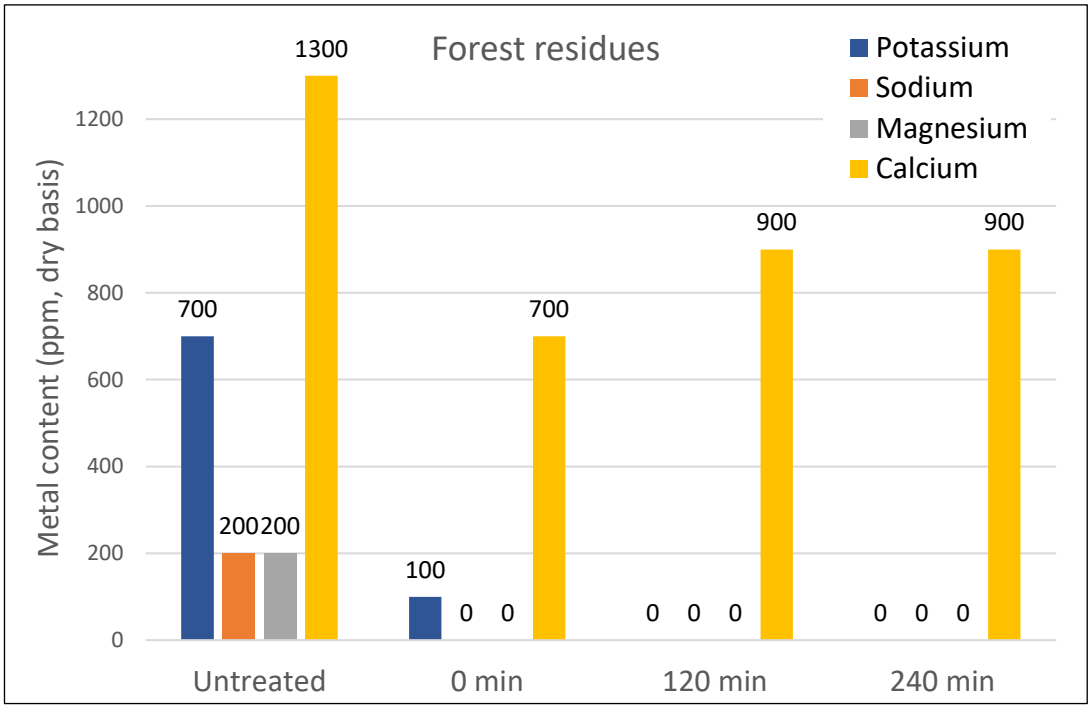

Figure 23. Alkali and alkaline earth metal content of forest residues before and after washing with washing times of 0, 120 and 240 minutes at 50 °C with biomass to water ratio of 1:10.

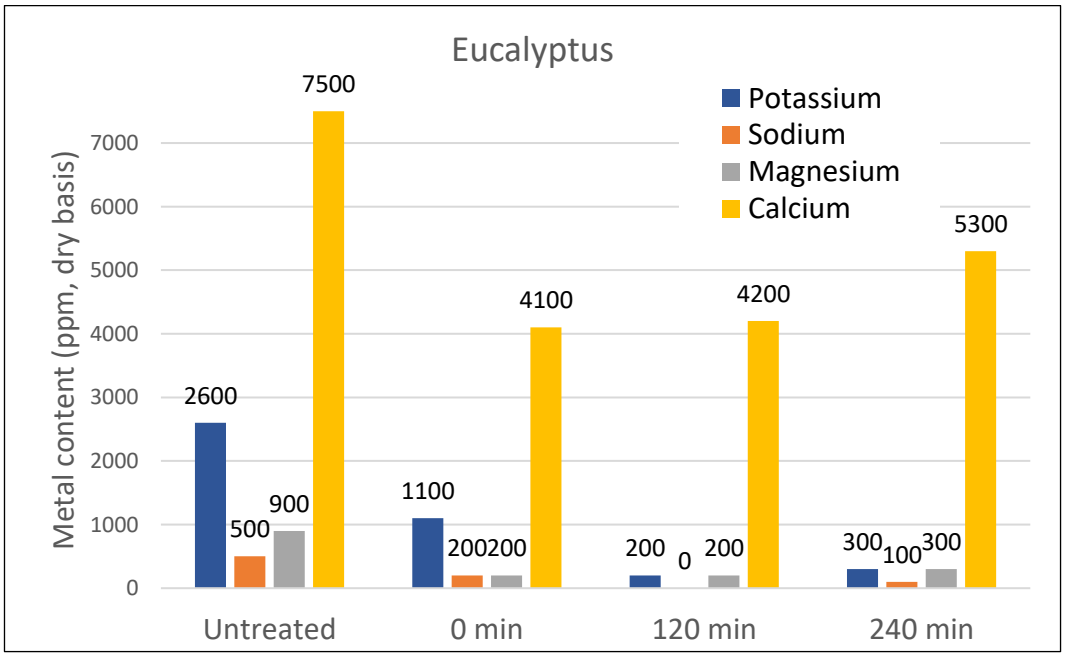

Figure 24. Alkali and alkaline earth metal content of eucalyptus before and after washing with washing times of 0, 120 and 240 minutes at 50 °C with biomass to water ratio of 1:10.

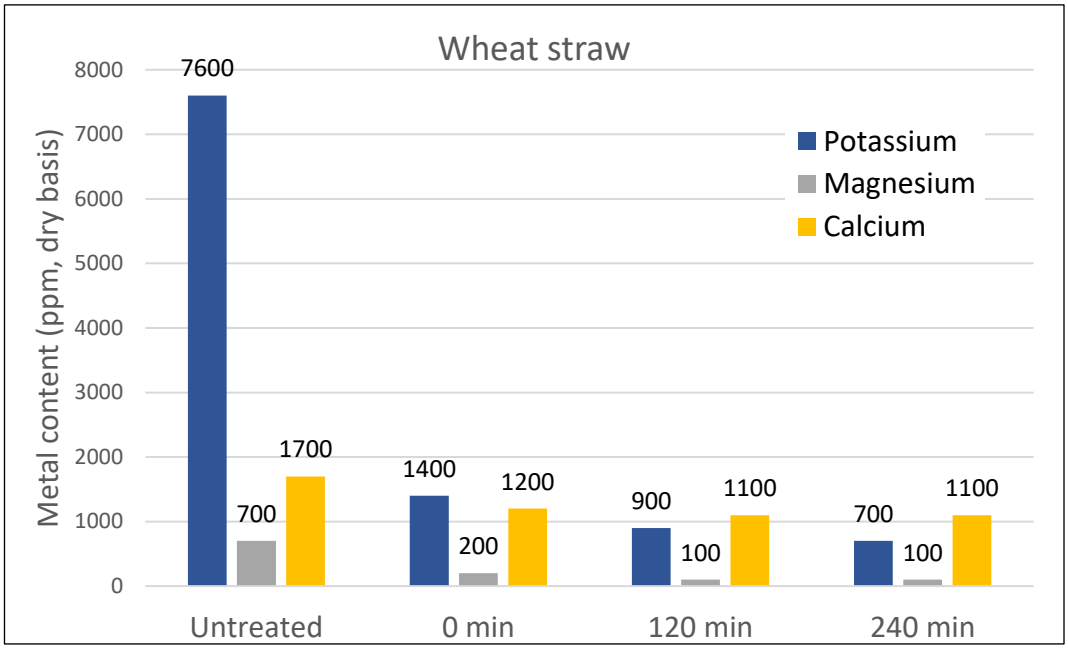

Figure 25. Alkali and alkaline earth metal content of wheat straw before and after washing with washing times of 0, 120 and 240 minutes at 50 °C with biomass to water ratio of 1:10.

The reason for enhanced calcium removal at higher temperature and elevated ash reduction with longer washing times might be that the more severe conditions deteriorate the structure of wood biomass so that the ash components become more accessible (Stefanidis et al. 2015). Reduced calcium content and increased TOC at elevated temperatures are indications of deteriorated cell structures, although increased dissolution of extractives can also increase TOC. Calcium is largely located in plant cell walls in ion-exchangeable form, interacting mainly with pectins and hemicelluloses. These both component groups include largely water-soluble polysaccharides, which may be broken down and dissolved when cell structures are disturbed. Calcium can possibly dissolve as free ions after the disruption of cell wall or with the organic matter if the bonding is strong enough. In addition, calcium in mineral form can be more soluble when temperature is increased.

Interestingly, the higher temperature did not have such clear effects on calcium removal with wheat straw and total ash content was reduced only at 80 °C. The

reason for this might be the different anatomical structure and chemical composition of agricultural straws compared to woody biomasses. In addition, water-soluble alkali metals in wheat straw were in easily removable form, majority of them being removable already by rinsing, which indicates that mass transfer limitations are less significant in straws. One reason for this may be that the nutrient rich parenchyma cells are concentrated at the inner surfaces of hollow straws where they are more accessible than in woods (Willför et al. 2011).

Overall, reductions in total ash were low with eucalyptus and wheat straw, although similar results have been published in the literature (Stefandis et al. 2015). Ash removal was in average 36.6 %, 18.8 % and 12.1 % for forest residues, eucalyptus and wheat straw, respectively. Corresponding results with 240 min washing time in 50 °C gave ash removals of 45.7 %, 22.8 % and 15.2 %, respectively. Ash reduction of forest residues was decent, but due to its low initial ash content, washing of it was not considered in further water washing experiments. One reason for lower removal efficiencies obtained in our experiments compared to results published in the literature might be that many studies have used fine (< 0.5 mm) particles in washing experiments (Mourant et. al 2011, Stefanidis et al. 2015). Washing of smaller particles can be more efficient (Turn et al. 1997). Small diameter reduces the mass transfer limitations and heavy grinding can deteriorate the cell structure more, which may enhance the washing rates and efficiencies especially with woody biomasses. In addition, variations in raw materials can be substantial.

8.5.3 Acid washing experiments

When washing liquid was changed to nitric acid, significant improvements in washing efficiency were observed with forest residues and eucalyptus, but effects were milder with the wheat straw. Ash removals obtained with 1 w-% nitric acid at 50 °C and 2 h washing time were 84.6 %, 43.4 % and 17.2 % for forests residues, eucalyptus and wheat straw, respectively. Ash contents of differently washed raw materials are presented in Figure 26. Studied parameters in acid washing

experiments were temperature, washing time, acid concentration, the amount of washing liquid and the water quality (deionized water vs. tap water).

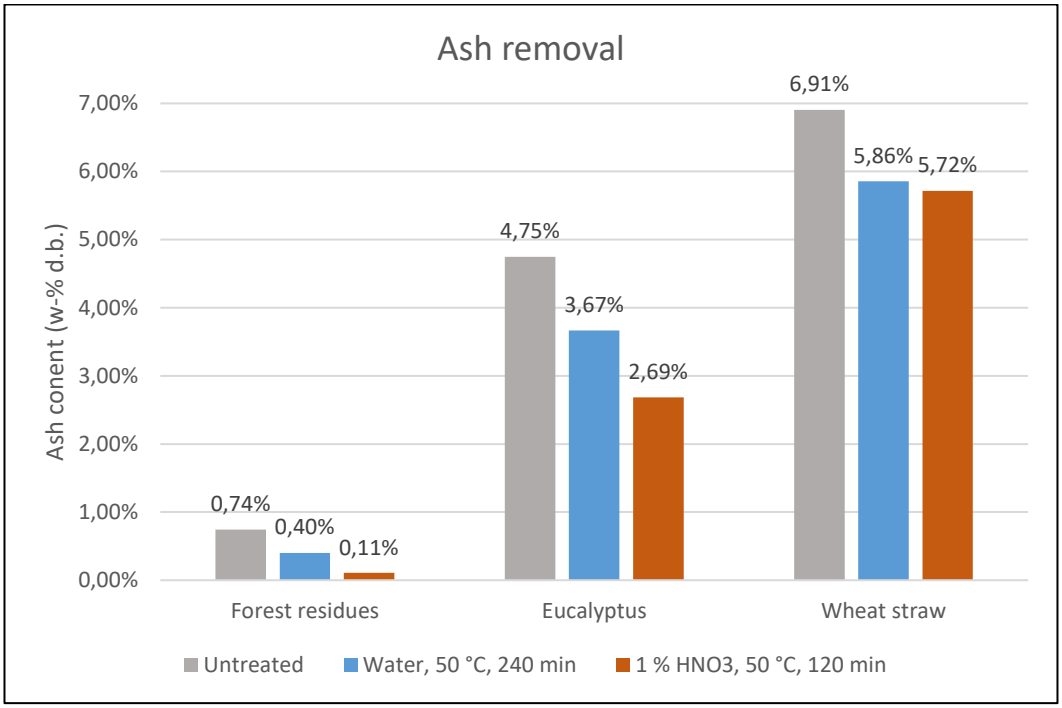

Figure 26. Ash content of untreated raw materials and ash contents after water washing and 1 w-% nitric acid washing with biomass to water ratio of 1:10.

Regarding the temperature in acid washings, total ash removal efficiency of eucalyptus improved clearly, when 50 °C temperature was used instead of room temperature. In the case of forest residues, only slight improvement was observed. Wheat straw did not show improved removal efficiency at elevated temperature. Increasing temperature had varying effects to AAEM removal. Calcium removal of eucalyptus was significantly enhanced in elevated temperature. However, rather large amount of calcium was still left in eucalyptus after washing at 50 °C, while all of the calcium of forest residues and wheat straw was removed already at room temperature. Stefanidis et al. (2015) reported similar results from the persistency of calcium in eucalyptus. In the case of wheat straw, small amount of potassium was retained but magnesium and calcium were removed completely. In the case of forest residues, concentrations of all AAEMs were reduced below the detection limit already at room temperature. However,

it should be emphasized that the initial ash content of forest residues was very low. AAEM contents of eucalyptus and wheat straw after acid washings can be seen in the Figures 27 and 28.

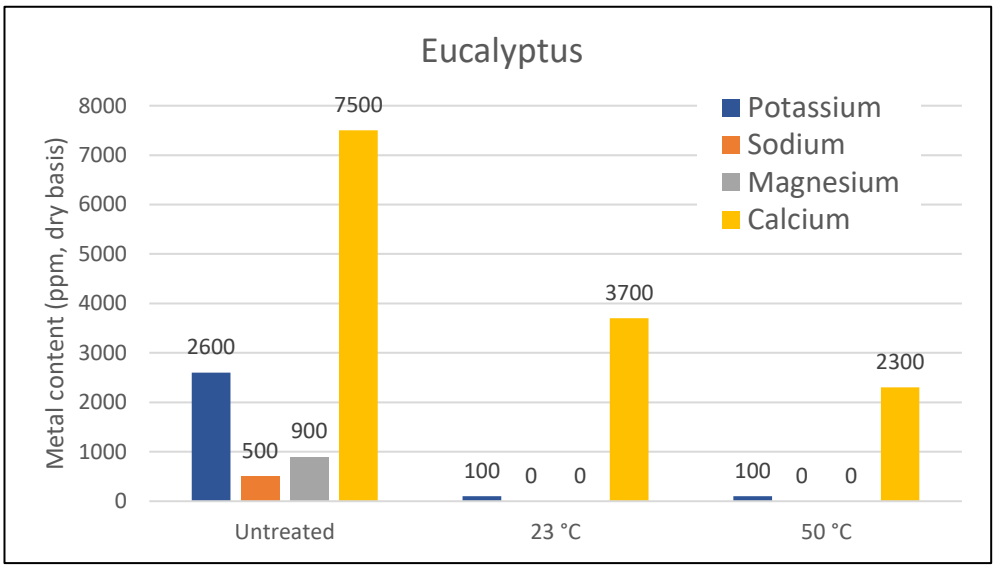

Figure 27. Alkali and alkaline earth metal contents of eucalyptus before and after washing with 1 w-% nitric acid solution at room temperature and at 50 °C, with biomass to washing liquid ratio of 1:10.

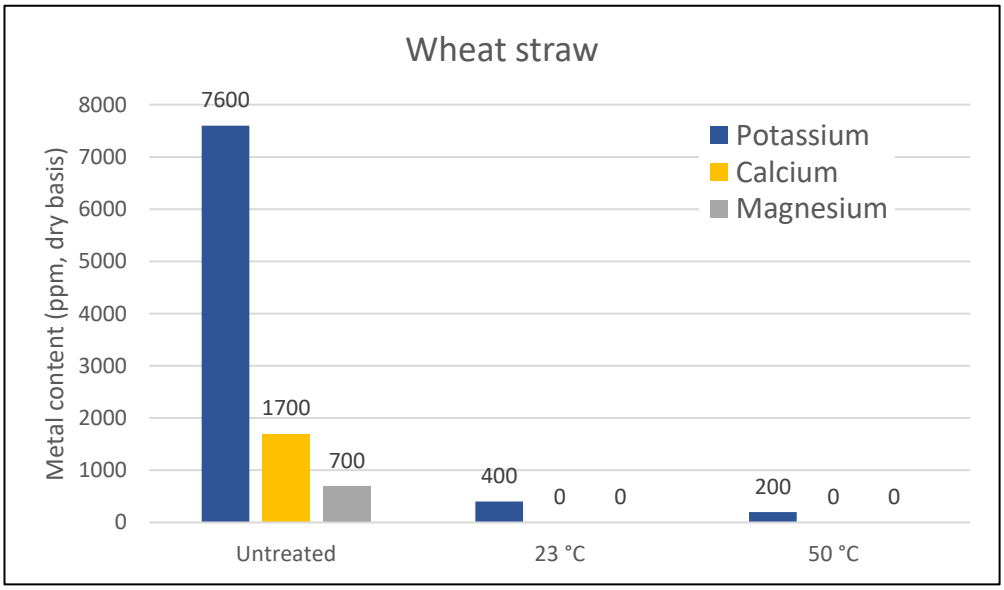

Figure 28. Alkali and alkaline earth metal contents of wheat straw before and after washing with 1 w-% nitric acid solution at room temperature and at 50 °C, with biomass to washing liquid ratio of 1:10.

Washing time was shown not to have drastic effects in acid washing. Similar results were obtained in 30 min and 120 min washing tests. In the case of eucalyptus and forest residues, minor decrease was seen on total ash removal efficiency, but results were still within the error margin of TGA. With straw, no change at all was observed with changing washing time. In addition, AAEM concentrations in washed raw materials were only slightly affected. Only significant difference was seen on the calcium content of eucalyptus that was reduced slightly less with shorter washing time. Thus, washings experiments were continued with reduced washing time.

TOC of washing liquid in acid washings did not increase compared to similar conditions in water washing experiments. However, TOC correlated in a similar manner with washing temperature and to some extent with washing time as in water washing experiments.

When the nitric acid concentration was reduced to 0.5 w-%, the total ash reduction decreased significantly with forest residues and eucalyptus and no lower concentrations were tested. Again, calcium content of eucalyptus was affected most with decreasing acid concentration. In addition, calcium reduction in forest residues was slightly decreased, but other AAEMs were totally removed.

Regarding the total ash reduction in wheat straw, 0.5 w-% acid concentration was as efficient as 1 w-% concertation even at room temperature and when the concentration was further decreased to 0.1 w-% the results were still the same within the error margin of TGA. However, calcium content of washed wheat straw was found to increase with decreasing acid concentration, but the observed differences were minor if total ash content is considered. The effect of acid concentration on eucalyptus and wheat straw can be seen in the Figures 29 and 30.

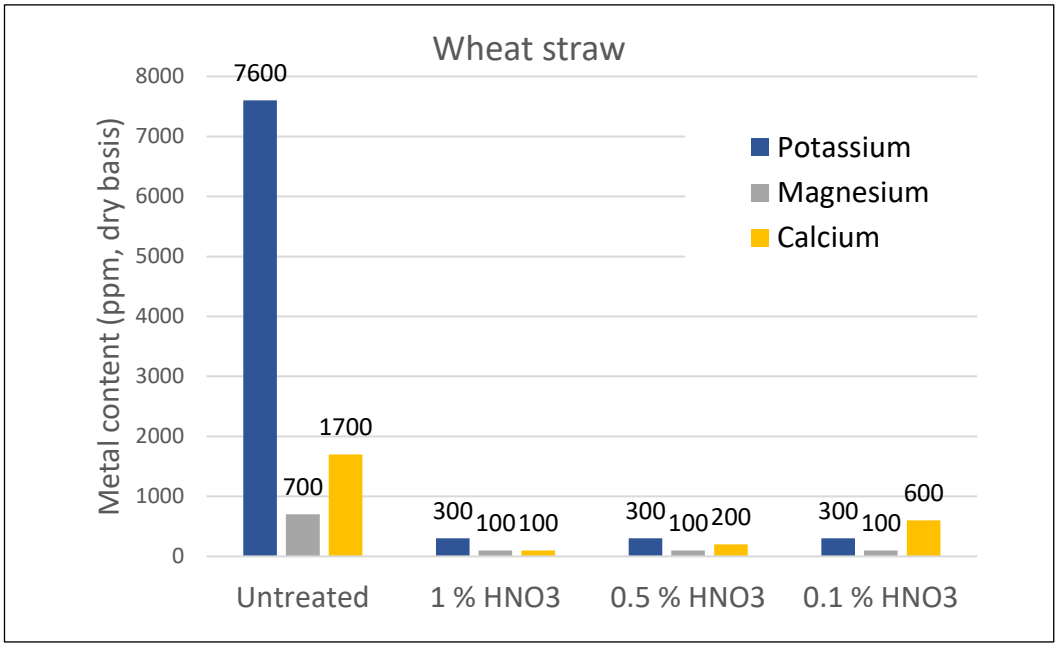

Figure 29. Alkali and alkaline earth metal content of wheat straw before and after washing with varying nitric acid concentration with 30 min washing time at room temperature and 1:10 biomass to washing liquid ratio.

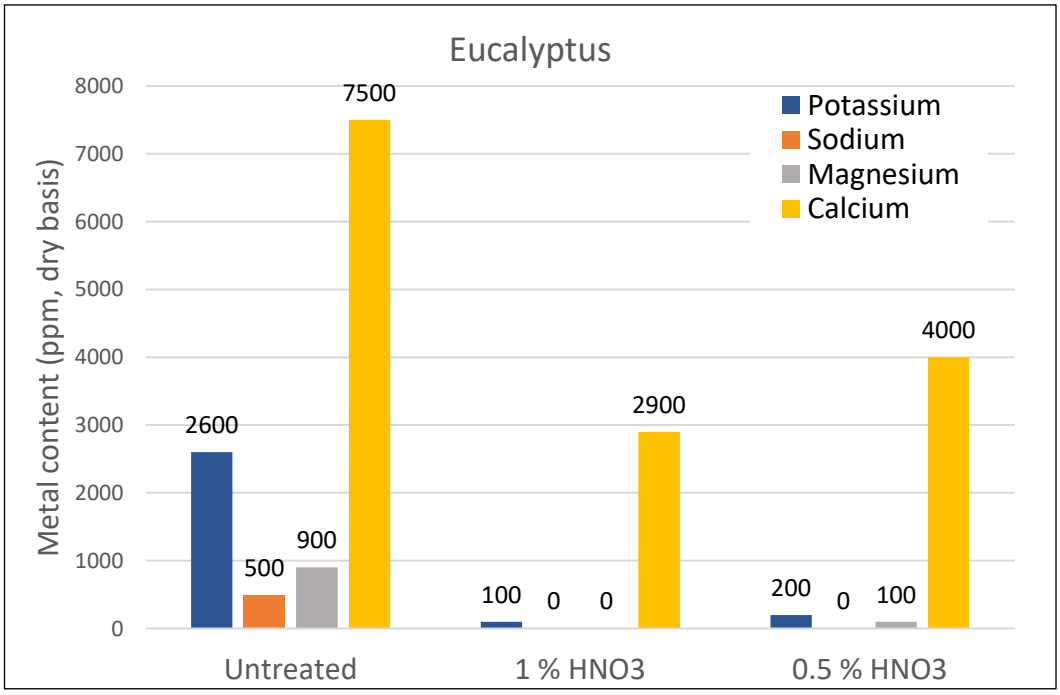

Figure 30. Alkali and alkaline earth metal content of eucalyptus before and after washing with varying nitric acid concentration with 30 min washing time at 50 °C and 1:10 biomass to washing liquid ratio.

Tap water was also tested in acid washing experiments with each raw material in their optimized washing conditions. Acidic washing liquid was made from tap water, and tap water was used in rinsing. With 30 min washing at 50 °C, ash removal efficiency of forest residues and especially eucalyptus were noticeably decreased. From AAEMs, calcium removal was affected the most. Total ash and AAEM removals were approximately at the same level as results obtained in 0.5 w-% nitric acid concentration. Washing wheat straw with 0.1 w-% nitric acid at room temperature for 30 min resulted in the same ash content independent of the quality of water. However, calcium removal was noticeably lowered also with the wheat straw when tap water was used instead of deionized water.

Tap water can reduce the washing efficiency by two mechanisms. First, the presence of other anions and cations in acidic washing liquids can disturb the operation of the acid during washing, e.g. by formation of salts and by electrostatic interactions between the species. Other option is that cations are removed from the anionic biomass during the mixing, but when acid traces are rinsed away, cations present in the rinsing water are attached again to these anionic sites.

Finally, reduced amount of washing liquid was tested with wood biomasses. Ratio of biomass to water was 1:5. The washing time at 50 °C was 30 min. Ash removal from forest residues was unaffected by the amount of the washing liquid. However, in the case of eucalyptus, ash removal was decreased considerably with the smaller amount of the washing liquid. In this case, the ash removal efficiency was at the same level with the efficiency at lower acid concentration and at the room temperature. Calcium removal was reduced significantly, but reduction of other AAEMs was not affected. Perhaps the proper wetting of the particles was compromised with lower amount of liquid and short washing time. Wetting can be crucial regarding the removal of ion-exchangeable cations such as calcium located within the cell walls. Another option is that the reduced amount of liquid reduces crucially the amount of available hydrogen cations to replace the ion-exchangeable metal cations which compromises the washing efficiency. For

example, only the AAEM content of eucalyptus is capable to neutralize 68 % of the acid when biomass to washing liquid ratio is 1:5 and acid concentrations is 1 %. Same value with forest residues is 13 %.

Overall, ash and AAEM removal was more efficient with acidic washing liquid as was expected. Acids are capable to remove the ion-exchangeable cations and mineral species that are soluble in acidic conditions (Davidsson et al. 2002). Interestingly, when washing parameters were changed, mainly calcium removal was affected. One explanation can be that e.g. potassium is removed prior to calcium due to its monovalent nature, when divalent calcium, removed as $Ca(NO_3)_2$, consumes more acid and is removed after the more removable species. Location of cations can also have effect. For example, calcium is largely located in the middle lamellae (Brelid et al. 1998). This can increase the mass transfer limitations because washing liquid needs to penetrate through cell walls to reach these locations.

Although total ash removal was enhanced with acidic washing liquids and AAEMs were almost completely removed, significant portion of ash was still left in washed samples. Low total ash reduction of wheat straw can be expected to result from its high silicon content. Silicon as a form of silica acts as structural reinforcement in many agricultural straws and it is poorly removed by washing (Jenkins et al. 1996, Turn et al. 1997). Silicon content of eucalyptus was also rather high and it is also expected to be in insoluble form. However, silicon can be expected to be inert element during the pyrolysis and retain largely in pyrolysis char (Carpenter et al. 2014). In addition, iron and aluminum contents of eucalyptus were larger compared to other two raw materials. These metals have been shown to be more resistant to water and acid washing than AAEMs (Stefanidis et al. 2015). With forest residues, content of these ash components was much lower, and fraction of AAEMs larger. Thus, the relative reduction in total ash was also the highest.

8.5.4 Washing experiments in bench scale

Washing conditions chosen for bench scale experiments, with the obtained washing results, are presented in Table 7. Choosing of conditions was based on the total ash and AAEM removal efficiencies. High acid concentration and temperature were used with both wood biomasses to ensure good ash removal, although milder conditions could be sufficient with forest residues used in our experiments. With wheat straw, milder conditions were chosen because higher temperature and acid concentration had no significant effects in laboratory experiments. For practical reasons, lower amount of rinsing water was used.

Table 7. Conditions and total ash after washing in bench scale experiments.

Sample	T (°C)	Washing water (B:W)	t (min)	Rinsing water (B:W)	Ash after washing	Lab scale results
Forest residues	50	1:10	30	1:10	0.29 %	0.22 %
Eucalyptus	50	1:10	30	1:10	2.54 %	2.81 %
Wheat straw	20	1:10	30	1:10	4.97 %	5.70 %

Total ash removals obtained with wood biomasses were well in line with laboratory experiments. However, total ash removal of wheat straw was more efficient than in large scale. Removal efficiencies of AAEMs were at same levels as in laboratory scale even with the wheat straw, although the calcium of eucalyptus was unreasonably low and can be expected to be a result of measurement error. Despite the anomalies in obtained results, the bench scale equipment was proven to work efficiently with ash reduction and AAEM removal. AAEM analysis of washed raw materials are presented in Table 8.

Table 8. Elemental analysis of raw materials after washing in bench scale.

Raw material	K	Na	Ca	Mg
Forest residues	< 50	< 50	< 50	< 50
Eucalyptus	400	100	800	100
Wheat straw	300	< 50	100	< 50

9 Conclusions

As the demand for sustainable biofuels and biochemicals grows, more and more interest towards utilizable, non-edible and renewable waste streams awakens. Fast pyrolysis is a robust and rather simple liquefaction technique of solid feedstocks to high energy density liquid bio-oil. However, decreasing quality of feeds introduces the need for their pretreatment. Especially feedstocks with high ash content have been demonstrated to cause several problems during processing. Inorganic, ash-forming elements, especially potassium, sodium, calcium and magnesium have been shown to possess catalytic activity, which results in decreased product yield and altered chemical composition of the produced bio-oil. In addition, higher inorganic content in the feedstock results in higher inorganic concertation in bio-oil, which is problematic from the scope of the further processing. Fortunately, majority of the most problematic and catalytically active ash components are removable either by water or acid treatment.

Various parameters of water and acid treatments were tested in the laboratory and bench scale experiments. Total ash content and concentrations of potassium, sodium, calcium and magnesium were monitored. Regarding the parameters of water washing, no significant changes in the total ash removal efficiency were observed when temperature, the amount of washing liquid or washing time were changed. The most significant parameter was found to be the acidity of the washing liquid.

Treatment of wood biomasses in dilute acids were significantly more efficient than treatment in pure water. Higher acid concentration was also more efficient than treatment in more dilute solutions. On the other hand, differences in total ash removal efficiencies between acid and water washings of wheat straw were minor. Acidic washing liquid was only slightly more efficient and increasing acid concentration had no clear effects. One reason for this is expected to be the high silicon content in wheat straw. Silicon is hardly soluble and removable by

conventional washing methods. However, silicon is considered catalytically as inert element during pyrolysis and its removal is not crucial.

Regarding the other studied parameters in acid washing, increasing temperature was found to enhance the washing efficiency with wood biomasses. In the case of wheat straw, room temperature was equally efficient. Short washing time was found to be as efficient as longer time with all raw materials in acidic conditions.

From the scope of the alkali and alkaline earth metal removal, calcium was the most persistent element. Potassium and sodium were largely removed by water in the case of all raw materials although lower concentrations were still reached with acid washing. Calcium and magnesium were persistent to water treatment but were removed in acid treatments. Removal of calcium was affected the most when parameters were altered. Calcium removal was decreased with decreasing acid concentration and temperature. Higher temperature probably deteriorates and breaks down plants' cell structure, which makes highly ion-exchangeable cations, such as calcium, more accessible.

Although the total ash removal of wheat straw was the lowest of the raw materials, it is probably the most potential feed for washing. Reasons for this include the high concertation of easily removable potassium and low concentration of persistent calcium, mildness of treatment conditions and results obtained which indicate that mass transfer limitations are less significant in the case of straw. Structure of straw differs from that of wood and washing of larger straw particles or even completely untreated straws may be suitable. This would make the process scheme more practical because it minimizes the need for grinding and drying. However, more information is needed from the behavior of untreated straw during washing and suitable technical solutions should be identified so that the need for washing liquids could be minimized. Utilization of pure water would be beneficial due to the reduced complexity of wastewater treatment. Creation of closed water system would be easier without acidic

washing liquids and process economics are enhanced when chemical consumption is minimized.

In addition, suitable AAEM levels in feeds and the effect of acid traces during the pyrolysis should be clarified from the scope of bio-oil yield and quality maximization so that appropriate washing method could be chosen. Altered chemical composition of oil and its benefits should be assessed and limits in metal content of bio-oil from the scope of further refining should be identified. Pyrolysis experiment in bench scale and eventually in pilot scale are recommended to clarify and demonstrate the benefits of de-ashed feeds in large scale.

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Appendix 1. Particle size distribution of sieved raw materials

Eucalyptus					
Mesh size	Sieve (g)	Sieve + Sample (g)	Sample (g)	Fraction (%)	Ash (w-% d.b.)
3.15	392.90	392.90	0	0.0	-
1.6	329.27	331.05	1.78	1.7	-
1	332.14	356.69	24.55	24.1	4.77 %
0.71	308.84	342.65	33.81	33.2	4.65 %
0.56	310.83	328.47	17.64	17.3	4.60 %
0.25	272.65	295.61	22.96	22.5	
0.106	266.91	267.93	1.02	1.0	-
Bottom	357.33	357.51	0.18	0.2	-
Total			101.94	100	4.60 %

Forest residues					
Mesh size	Sieves (g)	Sieve + Sample (g)	Sample (g)	Fraction (%)	Ash (w-% d.b.)
3.15	-	-	-	-	-
1.6	324.27	324.27	0	0.0	-
1	332.15	332.19	0.04	0.0	-
0.71	308.85	345.46	36.61	28.4	0.78 %
0.56	310.84	360.01	49.17	38.2	0.86 %
0.25	272.66	314.99	42.33	32.8	0.81 %
0.106	266.93	267.6	0.67	0.5	-
Bottom	357.33	357.38	0.05	0.0	-
Total			128.87	100	0.81 %

Wheat straw					
Mesh size	Sieves (g)	Sieve + Sample (g)	Sample (g)	Fraction (%)	Ash (w-% d.b.)
3.15	-	-	-	-	-
1.6	324.18	324.18	0	0.0	-
1	332.13	332.16	0.03	0.1	-
0.71	308.84	317.07	8.23	21.1	5.79 %
0.56	310.83	325.33	14.5	37.2	6.54 %
0.25	272.67	288.17	15.5	39.8	7.93 %
0.106	266.93	267.61	0.68	1.7	-
Bottom	357.33	357.33	0	0.0	-
Total			38.94	100	6.81 %

Appendix 2. Results from thermogravimetric analyses

Forest residues	Ash	Removal	T	W:B	Acid	Time
Sample	w-% d.b.	%	°C	ratio	w-%	min
Untreated	0.74 %	-	-	-	-	-
1 (DI-water)	0.52 %	29.74 %	23 °C	5:1	0 %	120
2 (DI-water)	0.42 %	42.91 %	50 °C	5:1	0 %	120
3 (DI-water)	0.47 %	36.90 %	80 °C	5:1	0 %	120
4 (DI-water)	0.43 %	41.36 %	23 °C	10:1	0 %	120
5 (DI-water)	0.42 %	43.64 %	23 °C	20:1	0 %	120
6 (DI-water)	0.62 %	16.28 %	23 °C	-	0 %	-
7 (DI-water)	0.51 %	31.05 %	50 °C	10:1	0 %	120
8 (DI-water)	0.40 %	45.72 %	50 °C	10:1	0 %	240
10 (tap water)	0.30 %	58.96 %	50 °C	10:1	1 %	30
11 (DI-water)	0.25 %	66.25 %	50 °C	5:1	1 %	30
12 (DI-water)	0.22 %	70.18 %	50 °C	10:1	1 %	30
13 (DI-water)	0.34 %	53.87 %	50 °C	10:1	0.5 %	30
14 (DI-water)	0.15 %	79.76 %	23 °C	10:1	1 %	120
15 (DI-water)	0.11 %	85.58 %	50 °C	10:1	1 %	120
Bench scale	0.29 %	79.76 %	50 °C	10:1	1 %	30

Eucalyptus	Ash	Removal	T	W:B	Acid	Time
Sample	w-% d.b.	%	°C	ratio	w-%	min
Untreated	4.75 %	-	-	-	-	-
1 (DI-water)	4.03 %	15.23 %	23 °C	5:1	0 %	120
2 (DI-water)	3.61 %	23.96 %	50 °C	5:1	0 %	120
3 (DI-water)	3.91 %	17.66 %	80 °C	5:1	0 %	120
4 (DI-water)	3.75 %	21.01 %	23 °C	10:1	0 %	120
5 (DI-water)	3.93 %	17.31 %	23 °C	20:1	0 %	120
6 (DI-water)	4.36 %	8.31 %	23 °C	-	0 %	-
7 (DI-water)	3.96 %	16.65 %	50 °C	10:1	0 %	120
8 (DI-water)	3.67 %	22.83 %	50 °C	10:1	0 %	240
10 (tap water)	3.12 %	34.31 %	50 °C	10:1	1 %	30
11 (DI-water)	3.27 %	31.09 %	50 °C	5:1	1 %	30
12 (DI-water)	2.81 %	40.92 %	50 °C	10:1	1 %	30
13 (DI-water)	3.16 %	33.46 %	50 °C	10:1	0.5 %	30
14 (DI-water)	3.14 %	33.93 %	23 °C	10:1	1 %	120
15 (DI-water)	2.69 %	43.47 %	50 °C	10:1	1 %	120
Bench scale	2.54 %	46.46 %	50 °C	10:1	1 %	30

Wheat straw	Ash	Removal	T	W:B	Acid	Time
Sample	w-% d.b.	%	°C	ratio	w-%	min
Untreated	6.91 %	-	-	-	-	-
4 (DI-water)	6.12 %	11.37 %	23 °C	10:1	0 %	120
5 (DI-water)	6.25 %	9.50 %	23 °C	20:1	0 %	120
7 (DI-water)	6.26 %	9.32 %	50 °C	10:1	0 %	120
9 (DI-water)	5.78 %	16.36 %	80 °C	10:1	0 %	120
6 (DI-water)	6.17 %	10.67 %	23 °C	-	0 %	-
8 (DI-water)	5.86 %	15.20 %	50 °C	10:1	0 %	240
16 (tap water)	5.82 %	15.77 %	23 °C	10:1	0.1 %	30
17 (DI-water)	5.77 %	16.42 %	23 °C	10:1	0.1 %	30
18 (DI-water)	5.70 %	17.39 %	23 °C	10:1	0.5 %	30
13 (DI-water)	5.67 %	17.82 %	50 °C	10:1	0.5 %	30
12 (DI-water)	5.61 %	18.74 %	50 °C	10:1	1 %	30
14 (DI-water)	5.63 %	18.50 %	23 °C	10:1	1 %	120
15 (DI-water)	5.72 %	17.24 %	50 °C	10:1	1 %	120
Bench scale	4.97 %	28.08 %	23 °C	10:1	0.5 %	30

Appendix 3. Results from elemental analyses of solid samples

Forest residues	K	Na	Ca	Mg	Si	Fe	Al	P	S	T	W:B	Acid	Time
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	°C	ratio	w-%	min
Untreated	700	200	1300	200	800	200	200	< 200	200	-	-	-	-
1 (DI-water)	100	< 50	1100	200	-	-	-	-	-	23 °C	5:1	0%	120
2 (DI-water)	< 50	< 50	1000	200	-	-	-	-	-	50 °C	5:1	0%	120
3 (DI-water)	< 50	< 50	700	100	-	-	-	-	-	80 °C	5:1	0%	120
4 (DI-water)	100	< 50	900	100	-	-	-	-	-	23 °C	10:1	0%	120
5 (DI-water)	< 50	< 50	1000	200	-	-	-	-	-	23 °C	20:1	0%	120
6 (DI-water)	100	< 50	700	< 50	-	-	-	-	-	23 °C	-	0%	-
7 (DI-water)	< 50	< 50	900	< 50	-	-	-	-	-	50 °C	10:1	0%	120
8 (DI-water)	< 50	< 50	900	< 50	-	-	-	-	-	50 °C	10:1	0%	240
10 (tap water)	< 50	100	< 50	< 50	-	-	-	-	-	50 °C	10:1	1%	30
11 (DI-water)	< 50	< 50	100	< 50	-	-	-	-	-	50 °C	5:1	1%	30
12 (DI-water)	< 50	< 50	100	< 50	-	-	-	-	-	50 °C	10:1	1%	30
13 (DI-water)	< 50	< 50	100	< 50	-	-	-	-	-	50 °C	10:1	0.5%	30
14 (DI-water)	< 50	< 50	< 50	< 50	-	-	-	-	-	23 °C	10:1	1%	120
15 (DI-water)	< 50	< 50	< 50	< 50	-	-	-	-	-	50 °C	10:1	1%	120
Bench scale	< 50	< 50	< 50	< 50	-	-	-	-	-	50 °C	10:1	1%	30

Eucalyptus	K	Na	Ca	Mg	Si	Fe	Al	P	S	T	W:B	Acid	Time
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	°C	ratio	w-%	min
Untreated	2600	500	7500	900	6000	800	1200	< 200	400	-	-	-	-
1 (DI-water)	600	100	6500	500	-	-	-	-	-	23 °C	5:1	0%	120
2 (DI-water)	400	100	6200	500	-	-	-	-	-	50 °C	5:1	0%	120
3 (DI-water)	200	< 50	5300	400	-	-	-	-	-	80 °C	5:1	0%	120
4 (DI-water)	600	100	5500	500	-	-	-	-	-	23 °C	10:1	0%	120
5 (DI-water)	500	100	6300	500	-	-	-	-	-	23 °C	20:1	0%	120
6 (DI-water)	1100	200	4100	200	-	-	-	-	-	23 °C	-	0%	-
7 (DI-water)	200	< 50	4200	200	-	-	-	-	-	50 °C	10:1	0%	120
8 (DI-water)	300	100	5300	300	-	-	-	-	-	50 °C	10:1	0%	240
10 (tap water)	100	100	3400	100	-	-	-	-	-	50 °C	10:1	1%	30
11 (DI-water)	100	< 50	4600	100	-	-	-	-	-	50 °C	5:1	1%	30
12 (DI-water)	100	< 50	2900	< 50	-	-	-	-	-	50 °C	10:1	1%	30
13 (DI-water)	200	< 50	4000	100	-	-	-	-	-	50 °C	10:1	0.5%	30
14 (DI-water)	100	< 50	3700	< 50	-	-	-	-	-	23 °C	10:1	1%	120
15 (DI-water)	100	< 50	2300	< 50	-	-	-	-	-	50 °C	10:1	1%	120
Bench scale	400	100	800	100	-	-	-	-	-	50 °C	10:1	1%	30

Wheat straw	K	Na	Ca	Mg	Si	Fe	Al	P	S	T	W:B	Acid	Time
Sample	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	°C	ratio	w-%	min
Untreated	7600	< 50	1700	700	17000	< 200	400	< 200	400	-	-	-	-
4 (DI-water)	1000	< 50	900	100	-	-	-	-	-	23 °C	10:1	0%	120
5 (DI-water)	1000	< 50	1100	100	-	-	-	-	-	23 °C	20:1	0%	120
7 (DI-water)	900	< 50	1100	100	-	-	-	-	-	50 °C	10:1	0%	120
9 (DI-water)	800	200	1100	100	-	-	-	-	-	80 °C	10:1	0%	120
6 (DI-water)	1400	200	1200	200	-	-	-	-	-	23 °C	-	0%	-
8 (DI-water)	700	< 50	1000	100	-	-	-	-	-	50 °C	10:1	0%	240
16 (tap water)	300	100	1000	100	-	-	-	-	-	23 °C	10:1	0.1%	30
17 (DI-water)	300	< 50	600	100	-	-	-	-	-	23 °C	10:1	0.1%	30
18 (DI-water)	300	< 50	200	100	-	-	-	-	-	23 °C	10:1	0.5%	30
13 (DI-water)	300	< 50	100	100	-	-	-	-	-	50 °C	10:1	0.5%	30
12 (DI-water)	300	< 50	100	100	-	-	-	-	-	50 °C	10:1	1%	30
14 (DI-water)	400	< 50	< 50	< 50	-	-	-	-	-	23 °C	10:1	1%	120
15 (DI-water)	200	< 50	< 50	< 50	-	-	-	-	-	50 °C	10:1	1%	120
Bench scale	300	< 50	100	< 50	-	-	-	-	-	23 °C	10:1	0.5%	30

Appendix 4. Results from total organic carbon analyses

Forest residues	TOC	TOC	T	W:B	Acid	Time
Sample	ppm	%	°C	ratio	w - %	min
1 (DI-water)	1855	0.19	23 °C	5:1	0 %	120
2 (DI-water)	2370	0.24	50 °C	5:1	0 %	120
3 (DI-water)	2650	0.27	80 °C	5:1	0 %	120
4 (DI-water)	945	0.1	23 °C	10:1	0 %	120
5 (DI-water)	525	0.05	23 °C	20:1	0 %	120
8 (DI-water)	1268	0.13	50 °C	10:1	0 %	240
10 (Tap water)	1223	0.12	50 °C	10:1	1 %	30
12 (DI-water)	1170	0.12	50 °C	10:1	1 %	30
14 (DI-water)	917	0.09	23 °C	10:1	1 %	120
15 (DI-water)	1372	0.14	50 °C	10:1	1 %	120

Eucalyptus	TOC	TOC	T	W:B	Acid	Time
Sample	ppm	%	°C	ratio	w - %	min
1 (DI-water)	3205	0.32	23 °C	5:1	0 %	120
2 (DI-water)	3805	0.38	50 °C	5:1	0 %	120
3 (DI-water)	5075	0.51	80 °C	5:1	0 %	120
4 (DI-water)	1290	0.13	23 °C	10:1	0 %	120
5 (DI-water)	635	0.06	23 °C	20:1	0 %	120
8 (DI-water)	1783	0.18	50 °C	10:1	0 %	240
10 (Tap water)	1544	0.15	50 °C	10:1	1 %	30
12 (DI-water)	1489	0.15	50 °C	10:1	1 %	30
14 (DI-water)	1070	0.11	23 °C	10:1	1 %	120
15 (DI-water)	1659	0.17	50 °C	10:1	1 %	120

Wheat straw	TOC	TOC	T	W:B	Acid	Time
Sample	ppm	%	°C	ratio	w - %	min
4 (DI-water)	2940	0.29	23 °C	10:1	0 %	120
5 (DI-water)	1580	0.16	23 °C	20:1	0 %	120
7 (DI-water)	3660	0.37	50 °C	10:1	0 %	120
9 (DI-water)	4350	0.44	80 °C	10:1	0 %	120
8 (DI-water)	4318	0.43	50 °C	10:1	0 %	240
16 (Tap water)	2699	0.27	23 °C	10:1	0.1 %	30
17 (DI-water)	2849	0.28	23 °C	10:1	0.1 %	30
18 (DI-water)	3330	0.33	23 °C	10:1	0.5 %	30
13 (DI-water)	3608	0.36	50 °C	10:1	0.5 %	30
12 (DI-water)	3688	0.37	50 °C	10:1	1 %	30
14 (DI-water)	3435	0.34	23 °C	10:1	1 %	120
15 (DI-water)	3782	0.38	50 °C	10:1	1 %	120